

# Report on Sea Water Desalination Analytical Procedures

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## FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

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## ACKNOWLEDGMENTS

The laboratory at Wrightsville Beach, North Carolina, provides analytical services for a number of research and development contractors. It soon became evident that standardization of analytical procedures was highly important when comparing the results and conclusions drawn from several pilot plant test programs. Since there were no standards for sea water, the Facility Manager directed the laboratory to undertake a continuing program of comparative evaluation and development of analytical procedures for use in the sea water conversion program. The work was started by Mr. William R. Sherwin, a chemist employed by Koppers Company, Inc. who provided M & O services for the station until December 1964. The work has been continued by the Facility Chemist, Mr. John R. Newton, and his assistant, Mr. Morris E. Atkins, who have developed and compiled the information for this first issue.

## INTRODUCTION

This publication has been compiled to provide analytical procedures which have been found applicable to sea water, brines, and product water. Research and development work was conducted at the Office of Saline Water's Wrightsville Beach Test Facility at Wrightsville Beach, North Carolina. In many cases, standard methods used to analyze industrial and fresh waters were found unsatisfactory when analyzing sea water. Methods were evaluated and modified, if necessary, until satisfactory procedures were obtained.

These methods have been modified to eliminate or compensate for interferences normally present in sea water. However, when using these methods, the analyst must realize that interferences not common to sea water may be present in samples due to corrosion of plant components or process additives. For example, copper may be present due to corrosion of copper components. If the concentration of copper exceeds the limit specified in the colorimetric determination of iron, it will interfere and must be removed prior to the iron determination.

The methods outlined include colorimetric, gravimetric, titrimetric, and instrumental methods of analysis. Detection limits are given if applicable. If amounts less than the detection limits are to be determined, concentration or extraction of the sample will be required. Methods of accomplishing this are discussed in detail in reference 4, Ch. 1, Sec. 26.

New methods of analysis, such as atomic absorption spectroscopy, will be added as they are developed.

## CHAPTER I. ANALYTICAL PROCEDURES FOR SEA WATER

## SECTION 1. DEFINITIONS OF TERMS RELATING TO SEA WATER

Absorbance	- The logarithm to the base 10 of the reciprocal of the relative transmittance, T. Absorbance thus expresses the excess absorption over that of a specified reference or standard.
Accuracy	- The degree of agreement between results of measurement and the true value for the property being measured.
Acid	- A compound which dissociates in water solution to furnish hydrogen ions.
Acidify	- To make acidic by the addition of acid or acid salt.
Acidity	- The quantitative capacity of aqueous media to react with hydroxyl ions.
Adsorption	- Physical adhesion of molecules to the surfaces of solids without chemical reaction.
Aliquot	- A measured fraction of the known total volume of a solution.
Alkalinity	- The quantitative capacity of aqueous media to react with hydrogen ions.
Analysis, chemical	- Determination of the chemical elements or constituents of a compound or mixture. Also a statement of the results of such a determination.
Anion	- A negatively charged ion resulting from dissociation of molecules in aqueous solution.
Anode	- The positive pole in an electrolytic cell which attracts negatively charged particles or ions (anions).
Ascarite	- A proprietary absorbent for carbon dioxide consisting of asbestos fibers impregnated with dehydrated sodium hydroxide.
Aspirator	- A type of suction pump operated from a laboratory water tap.
Basicity	- The quantitative capacity of aqueous media to react with hydrogen ions.
Beer's Law	- The degree of absorption of light depends on the thickness of the layer traversed and on the molecular concentration of colored substances in that layer.

BOD	- Biochemical oxygen demand of a water — the oxygen required for oxidation of the soluble organic matter by bacterial action in the presence of oxygen.
Brine	- Concentrated solution, especially of chloride salts.
Buffer	- A substance which tends to resist changes in pH of a solution.
Buffered water	- Water containing dissolved or suspended material which resists changes in the pH of the water.
Calibration	- The process of standardizing.
Carbonate hardness	- That hardness in a water caused by bicarbonates and carbonates of calcium and magnesium.
Cathode	- The negative pole of an electrolytic cell which attracts positively charged particles or ions (cations); the negative electrode of a vacuum tube.
Cation	- A positively charged ion resulting from dissociation of molecules in solution.
Chelating agents	- Chemical compounds which have the property of withdrawing ions into soluble complexes.
Chlorinity	- The chlorine-equivalent of the precipitated halides expressed in grams per kilogram of sea water.
Chlorosity	- The chlorine-equivalent of the precipitated halides expressed in grams per liter of sea water at 20° C.
Colloidal	- Matter of very fine particle size, usually in the range of $10^{-5}$ to $10^{-7}$ cm in diameter.
Colorimeter	- A device for measuring or comparing colors or colored solutions.
Colorimetric determination	- An analytical procedure based on measurement, or comparison with standards, of color naturally present in samples or developed by addition of reagents.
Comparator	- A device for comparing colored or turbid solutions against standard solutions' light filters under favorable lighting conditions.
Complexes	- Compounds formed by the union of two or more simple salts.
Concentration	- The process of increasing the dissolved solids per unit volume of solution, usually by evaporation of the liquid; the amount of material dissolved in a unit volume of solution.

Condensate	- Liquid (water) obtained by evaporation and subsequent condensation.
Condenser	- An apparatus for removing heat from a gas (steam) so as to cause the gas to revert to the liquid state (water).
Cooling coil	- A coil of pipe or tubing to contain a flowing stream of hot liquid which is cooled by heat transfer to a cold liquid outside.
Culture medium	- A food substance for growing organic life for study.
Deaeration	- The process of removing air from a liquid in which it is dissolved.
Decantation	- Separation of a liquid from solids, or from a higher density liquid, by carefully pouring off the upper layer after the heavier material has settled.
Decompose	- To separate into simpler substances or to change the form or quality of a substance by chemical action; to decay or rot.
Dehydrated	- Freed from, or lacking, water.
Density	- Weight per unit volume.
Detergent	- A cleaning and dispersing agent which, like soap, removes a film from its supporting structure by other means than solvent or chemical action.
Digestion	- Prolonged solution of, or reaction with, a solid by a liquid.
Dilution	- The addition of more solvent to a solution.
Dissolved matter	- The material in solution in a liquid.
Effluent	- A liquid, solid, or gaseous product, frequently waste, discharged or emerging from a process.
Electrical Conductivity	- The reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specified temperature.
End point	- The stage in a titration when equivalence is attained as revealed by a change that can be observed or measured such as color development, formation of precipitate, or attainment of specified pH.
End point, electrometric	- The stage in a titration when equivalence is reached as revealed by attainment of a specified pH or change in current flow measured by a glass electrode.

Equivalent, chemical	- The weight in grams of a substance which combines with or displaces one gram of hydrogen, obtained by dividing the formula weight by the valence.
Evaporated	- A liquid converted to its vapor by the application of heat or reduced pressure.
Evolution	- The escape or liberation of a gas.
Extraction	- The process of dissolving and separating out specific constituents of a sample by treatment with solvents specific for those constituents.
Equivalent per Million (epm)	- A unit chemical equivalent weight of solute per million unit weights of solution.
Filtrate	- The liquid which has passed through a filter.
Filtration	- The process of separating solids from a liquid by means of a porous substance through which only the liquid passes.
Glass electrode	- An electrode consisting of a thin glass membrane separating solutions of known and unknown pH value, the potential difference between the two sides being measured for determining the pH of the unknown.
Gravimetric	- Measured by weight.
Hardness	- A characteristic of water generally accepted to represent the total concentration of calcium and magnesium ions.
Hydrocarbon	- Compound consisting solely of carbon and hydrogen.
Hydrometer	- A buoyant instrument with graduated stem for measuring the specific gravity of liquids.
Index of refraction	- Ratio of the velocity of light in the substance in question to the velocity of light in a vacuum.
Indicator	- Substance which gives a visible change, usually of color, at a desired point in a chemical reaction.
Interfering substances	- Materials which restrict or prevent a desired reaction, or contaminate the product.
Ion	- An atom or radical in solution carrying an integral electrical charge either positive (cation) or negative (anion).
Membrane, porous	- A barrier, usually thin, which permits the passage only of particles up to a certain size or special nature.
Nephelometry	- Measurement of the light scattered by turbid liquids.

Nessler tubes	- Matched cylinders with strain-free, clear-glass bottoms for comparing color density or opacity.
Neutralization	- Reaction of acid or alkali with the opposite reagent until the hydrogen ions are approximately equal to the hydroxyl ions in the solution.
Noncarbonate hardness	- Hardness in water caused by chlorides, sulfates, and nitrates of calcium and magnesium.
Oxidation	- Reaction of a substance with oxygen; loss of electrons by one element to another element.
Oxide	- A chemical compound of a metal, or group of elements which act in common as a metal, with oxygen.
Part per Billion (ppb)	- A measure of proportion by weight, equivalent to a unit weight of solute per billion ( $10^9$ ) unit weights of solution.
Part Per Million (ppm)	- A measure of proportion by weight and equivalent to a unit weight of solute per million unit weights of solution.
pH	- A measure of the hydrogen ion concentration of a sample and representing the logarithm to the base 10 of the reciprocal (negative logarithm) of the activity of hydrogen ions.
Photometer	- An instrument which measures the intensity of light or degree of light absorption.
Physical tests	- Determination based on observation or measurement of physical properties.
Precipitate	- An insoluble compound formed by chemical reaction between two or more normally soluble compounds in solution.
Precision	- The degree of agreement of repeated measurements of the same property, expressed in terms of dispersion of test results about the arithmetical mean result obtained by repetitive testing of a homogeneous sample under specified conditions.
Qualitative	- Pertaining to the nature of component parts rather than to the amount of such components present.
Quantitative	- Pertaining to the amount of component parts present.
Residual Chlorine (Chlorine Residual)	- The amount of available chlorine present in industrial water at any specified period, subsequent to the addition of chlorine.
Residue	- That which remains after a part has been separated or otherwise treated.

Sensitivity	- The least amount or concentration that can be detected, not determined, by a method.
Solubility	- Degree to which a substance will dissolve in a particular solvent.
Solutes	- Substances which are dissolved in a liquid.
Specific gravity	- Ratio of the weight of any volume of a substance to the weight of an equal volume of water at 4°C.
Spectrophotometry	- Quantitative measurement with a photometer of the quantity of light of any particular wavelength absorbed by a colored solution, or emitted by a sample subjected to some form of excitation such as a flame, arc, or spark.
Surface-Active Agent (Surfactant)	- Substance that affects (usually reduces) surface tension when dissolved in water solution, or which similarly affects interfacial tension between two liquids.
Suspended Matter (Suspended Solids)	- That matter (those solids) which can be separated from the sample by filtration.
Turbidimeter	- Instrument for determining the quantity of matter, in the form of fine suspended particles, in a liquid.
Turbidity	- The reduction of transparency of a liquid due to the scattering of light by suspended particles.
Volatile	- Capable of being readily evaporated at relatively low temperature.
Volatilize	- To convert into a gas or vapor.
Volumetric	- Pertaining to measurement by volume, as opposed to gravimetric.

## SECTION 2. REPORTING RESULTS

### 1. Scope

This section outlines items which shall be included, if available, when reporting results obtained by methods covered in this manual.

## 2. Items to be Reported

### a. Sample Identification

- (1) Name of Contractor
- (2) Contractor sample identification
- (3) Plant conditions
- (4) Date sample taken
- (5) Analyses to be made
- (6) Date results needed

### b. Laboratory Identification

- (1) Lab test number
- (2) Date Submitted
- (3) Date analyses began
- (4) Date analyses completed
- (5) Man-hours required
- (6) Cost of special apparatus and/or chemicals
- (7) Analyst reporting results

### c. Test Results

Results are expressed as outlined under the Calculations paragraph of each method. The form used to report results shall be left to the discretion of the individual laboratory.

## SECTION 3. PHYSICAL TESTS

### A. pH of Sea Water

The most common method for determining the pH of sea water is with a pH meter and glass-calomel electrode system. Since this method is well-known, it will not be outlined here. The procedure is thoroughly covered in references 2 and 3, Ch. 1, Sec. 26. In reference 4, Ch. 1, Sec. 26, considerable information concerning the pH of sea water is found.

### B. Specific Conductance of Sea Water

The specific conductance of sea water is determined by measurement with a self-contained conductance instrument. Many types of instruments are

available commercially. A specific conductance cell with a cell constant of 1 is required. Procedures for measuring specific conductance are covered in references 2 and 3, Ch. 1, Sec. 26. In reference 4, Ch. 1, Sec. 26, considerable information concerning the specific conductance of sea water is found.

### C. Specific Gravity of Sea Water

Methods for determining specific gravity include weighing, hydrometers, balance suspended plummet, etc. For approximate work, a hydrometer in the proper range is satisfactory. The measurement of the specific gravity of sea water has become less important due to the difficulty in obtaining a precise value and other methods for determining total dissolved solids. Considerable information on the specific gravity of sea water is found in reference 4, Ch. 1, Sec. 26.

### D. Salinity of Sea Water

Salinity is the total amount of solid material in grams per kilogram of sea water when all carbonate has been converted to oxide, bromine and iodine replaced by chlorine, and all organic matter completely oxidized. The salinity of sea water is arrived at by determining the chlorosity as outlined in Ch. 1, Sec. 10 or Sec. 11, converting to chlorinity (see curve, Figure 1), and using the following equation:

$$\text{Salinity} = 1.8147 \times \text{Chlorinity}$$

### E. Temperature

Temperature measurements are made with mercury filled thermometers. The thermometer should be checked occasionally against a NBS certified thermometer. The temperature is expressed in degrees Fahrenheit or centigrade and is reported to the nearest one-tenth degree.

### F. Turbidity of Sea Water

Turbidity may be determined by using a candle turbidimeter, photometer, nephelometer, or other more exotic instruments. A nephelometer such as the Hellige Turbidimeter has been found satisfactory for sea water. Recording turbidimeters of various types are also available. Procedures for determining turbidity using these instruments are well-known and therefore will not be outlined.

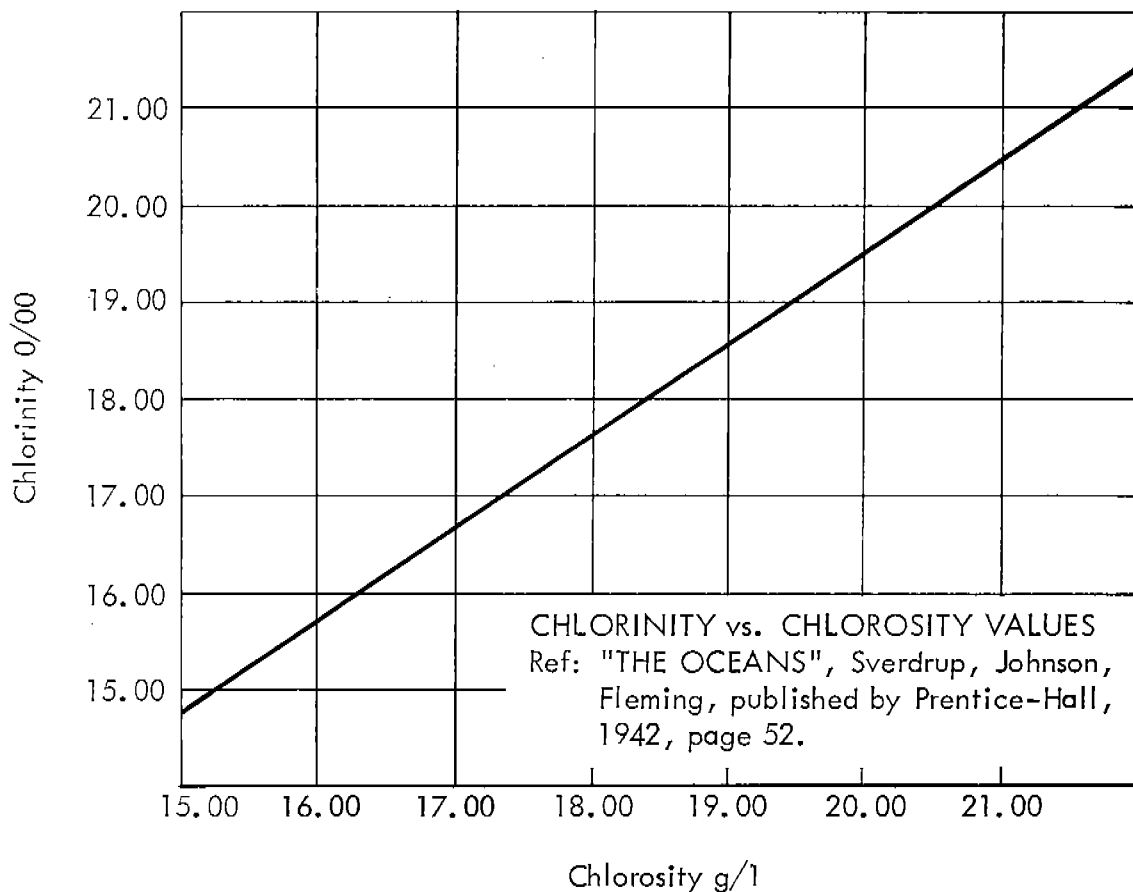


Figure 1

#### SECTION 4. ALKALINITY, HARDNESS, AND NONCARBONATE HARDNESS IN SEA WATER

##### 1. Scope and Application

This method covers the determination of alkalinity, hardness, and noncarbonate hardness in sea water. The method is applicable to sea water and product water.

##### 2. Principle of Method

Alkalinity is a measure of the bicarbonate, carbonate, and hydroxide components of water. It is determined by titration with a standard acid to a specified pH.

Hardness is generally accepted to represent the concentration of calcium and magnesium ions in water. It is determined by either calculation from known ion concentrations or by EDTA titration. In the titration method, ethylenediamine tetraacetic acid and its sodium salts form a chelated, soluble complex when added to a solution containing certain metal cations. An indicator is added to the sample containing calcium and magnesium ions at a specified pH. When EDTA is added as the titrant, the calcium and magnesium are complexed. Other ions will contribute hardness (see paragraphs 3 and 9b below).

Hardness equivalent to total alkalinity is called "carbonate hardness." The amount of hardness in excess of this is called "noncarbonate hardness." A method of calculating "noncarbonate hardness" is outlined.

### 3. Interferences

The method for determining alkalinity in sea water is essentially free of interferences. When determining hardness in sea water, strontium is titrated with calcium. However, the amount of strontium present in sea water will not cause a significant error due to the relatively high concentration of calcium. Other cation interferences such as aluminum, barium, iron, manganese, and zinc are removed. Anion interferences are negligible.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

a. Fisher Titrimeter with standard reference and glass electrode for pH measurement.

b. Miscellaneous Glassware - burets, flasks, beakers, etc.

### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

### 7. Reagents

a. Standard acid, 0.02N: Add 0.56 ml conc.  $H_2SO_4$  to 100 ml reagent water and dilute with reagent water to 1 liter. Conc. HCl (1.70 ml) may be used.

b. Thioacetamide, 1M: Dissolve 7.5 g  $\text{CH}_3\text{CSNH}_2$  in 100 ml reagent water.

c. EDTA Titrant, 0.01M: Dissolve 3.723 g of disodium ethylenediamine tetraacetate dihydrate in reagent water and dilute to 1 liter. Standardize against standard calcium solution. Adjust to 1 ml = 1 mg  $\text{CaCO}_3$ .

d. Buffer Solution: Dissolve 16.9 g  $\text{NH}_4\text{Cl}$  in 143 ml conc.  $\text{NH}_4\text{OH}$ . Add 1.25 g EDTA magnesium salt (tetraacetic acid magnesium disodium salt) and dilute to 250 ml with reagent water.

e. Eriochrome Black T Indicator: Dissolve 0.5 g dye and 4.5 g hydroxylamine hydrochloride in 100 ml 95% ethyl alcohol.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Procedure

### a. Alkalinity

Add 100 ml of the sample to a 250 ml beaker containing a teflon coated stirring bar. Check the pH of the sample using a pH meter. Place the beaker on the magnetic stirrer of the Fisher Titrimeter. Zero the titrimeter and then with the electrodes in the sample, set the meter to the sample pH. (See Note 1.) Adjust the magnetic stirrer to mix as rapidly as possible without splashing. Set the calibrated dial on 4.5 and titrate the sample with 0.02N acid using smaller increments as the end point is approached. Record the ml of acid required.

NOTE 1 - Turn power switch on and allow at least 5 minutes for warm-up. To zero the meter, set the operation switch to the "zero" position and the function switch to "pH." Adjust the null meter to zero with the zero with the zero adjust switch. To set the sample pH, turn the operation switch to the "use" position and set the sample pH on the calibrated dial.

### b. Hardness

Dilute 5 ml of the sea water sample to 10 ml with reagent water. Add 1 ml of 1M thioacetamide solution and heat without boiling. Cool and filter through a #42 Whatman filter paper. Add buffer solution dropwise to pH 10 and heat without boiling. Cool and filter through a #1 Whatman filter paper. Dilute to 50 ml with reagent water. Add 1/2 ml Eriochrome Black T indicator and titrate with 0.01M EDTA to the blue end point. This procedure in effect gives total calcium and magnesium hardness. By not precipitating other polyvalent cations with thioacetamide, hardness contributed from these ions can be determined. To calculate the contribution by these ions and Ca and Mg, multiply the concentrations (mg/l) by the following factors:

<u>Cation</u>	<u>Factor</u>	<u>Cation</u>	<u>Factor</u>
Ca	2.497	Al	3.710
Mg	4.116	Zn	1.531
Sn	1.142	Mn	1.822
Fe	1.792		

c. Noncarbonate Hardness

Determine by the equation given under the calculation section.

10. Calculations

a. Alkalinity (total as  $\text{CaCO}_3$ )

$$\text{Total alkalinity, ppm} = \frac{\text{ml acid} \times 1,000}{\text{ml sample}}$$

$$\text{Total alkalinity, epn} = \frac{N \times \text{ml acid} \times 1,000}{\text{ml sample}}$$

where N = normality of acid

b. Hardness (as  $\text{CaCO}_3$ )

$$\text{Hardness, ppm} = \frac{\text{ml EDTA} \times 1,000}{\text{ml sample}}$$

c. Noncarbonate Hardness

ppm noncarbonate hardness as  $\text{CaCO}_3$  = 50.05 (epn hardness - epn alkalinity)

$$\text{epn hardness} = \frac{20 \times \text{ml EDTA}}{\text{ml sample}}$$

epn alkalinity = See paragraph a above.

11. Precision and Accuracy

a. Alkalinity

Results are reproducible to 1 ppm and accurate to  $\pm 3$  ppm.

b. Hardness

Results are reproducible to 20 ppm.

## SECTION 5. BORON IN SEA WATER

### 1. Scope and Application

This method covers the colorimetric determination of boron in sea water. The method is applicable to the analysis of sea water and product water.

### 2. Principle of Method

Boron is determined colorimetrically by addition of a solution of carmine in concentrated sulfuric acid and measuring the color developed with a spectrophotometer. The color change is from bright red to a bluish red or blue depending on the boron concentration. Boron concentrations of 1-10 mg/l can be detected using this method.

### 3. Interferences

Ions normally present in sea water do not interfere with this method.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

- a. Spectrophotometer for use at 585 mμ.
- b. 2 ml pipet.
- c. 125 ml erlenmeyer flasks.

### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

### 7. Reagents

- a. Hydrochloric Acid (HCl), conc.
- b. Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>), conc.
- c. Carmine Solution: Dissolve 0.92 g of carmine N. F. 40 in 1 liter of conc. H<sub>2</sub>SO<sub>4</sub>.

d. **Standard Boric Acid Solution:** Dissolve 0.5716 g of  $\text{H}_3\text{BO}_3$  (reagent grade ACS) in reagent water and dilute to 1 liter. 1 ml of this solution equals 0.100 mg B. NOTE: Keep the reagent grade  $\text{H}_3\text{BO}_3$  tightly stoppered to prevent absorption of moisture.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Calibration and Standardization

Prepare a series of standards over the range of 0-10 mg/l boron using the standard boric acid solution. Treat 2.00 ml of the standards and a reagent water blank as outlined previously. Plot the measured absorbance against mg boron.

## 10. Procedure

Pipet 2.00 ml of the sample into a small erlenmeyer flask and add 2 drops of conc. HCl. Slowly add 10.0 ml of conc.  $\text{H}_2\text{SO}_4$ . Mix well and cool. Add 10.0 ml of the carmine solution, mix well, and allow to stand. After at least 45 minutes, measure the absorbance against a reagent water blank using a spectrophotometer at 585 m $\mu$ . Determine the ppm boron as outlined under Calculations.

## 11. Calculations

ppm boron is determined by comparison of observed absorbance with the calibration curve and using the following equation:

$$\text{mg/l B} = \frac{\text{mg B (from curve)} \times 1,000}{\text{ml sample}}$$

## 12. Precision and Accuracy

Results are accurate and reproducible to within  $\pm 0.4$   $\mu\text{g}$  boron.

## SECTION 6. BROMIDE AND IODIDE IN SEA WATER

### 1. Scope and Application

This method outlines the determination of bromide and iodide in sea water. The method is applicable to sea water and product water.

### 2. Principle of Method

Bromide and iodide ions are determined in sea water by titration with sodium thiosulfate. Iodide is oxidized to iodate by bromine and the iodine equivalent is liberated and titrated when potassium iodide is added. When iodide and bromide ions occur together, they are oxidized to iodate and bromate with hypochlorite. Iodine equivalent to combined iodate and bromate is liberated and titrated when potassium iodide is added. Bromide is determined by the difference in titrations.

### 3. Interferences

Iron, manganese, and organic matter interfere but are removed by treatment with calcium oxide.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

- a. Iodine flasks, 250 ml.
- b. Miscellaneous glassware.

### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

### 7. Reagents

a. Acetic Acid, 1:8: 1 volume glacial acetic acid diluted with 8 volumes of reagent water.

- b. Bromine Water, saturated (stored in glass-stoppered actinic glass bottle).
- c. Calcium Carbonate, powdered ( $\text{CaCO}_3$ ).
- d. Calcium Oxide, anhydrous powdered ( $\text{CaO}$ ).
- e. Hydrochloric Acid, 1:4: 1 volume conc.  $\text{HCl}$  diluted with 4 volumes of reagent water.
- f. Methyl Red Indicator: Dissolve 0.1 g methyl red in 100 ml reagent water.
- g. Potassium Fluoride, crystals ( $\text{KF} \cdot 2\text{H}_2\text{O}$ ).
- h. Potassium Hypochlorite Solution: Pass 35 g of bromine-free chlorine gas into a solution of 61.7 g potassium hydroxide dissolved in 1 liter reagent water. Continually stir and cool during addition of the chlorine gas. Store in a dark bottle.
- i. Potassium Iodide, crystals ( $\text{KI}$ ).
- j. Sodium Acetate Solution: Dissolve 275 g  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  in 1 liter reagent water and filter.
- k. Sodium Chloride, crystals ( $\text{NaCl}$ ).
- l. Sodium Formate Solution: Dissolve 50 g  $\text{NaHCO}_2$  in hot, reagent water and dilute to 100 ml.
- m. Sodium Molybdate Solution: Dissolve 1 g of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in 100 ml reagent water.
- n. Sodium Thiosulfate Stock Solution: Dissolve 25 g of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 1 liter reagent water. Add 1 g  $\text{Na}_2\text{CO}_3$  to preserve the solution.
- o. Sodium Thiosulfate Standard Solution: Dilute 100 ml of the stock solution to 1 liter with reagent water. Standardize the solution against potassium iodide solution (0.3567 g of recrystallized  $\text{KIO}_3$ , dried at  $180^\circ\text{C}$  for 2 hours, in 1 liter reagent water). Pipet 25 ml of  $\text{KIO}_3$  solution into a 250 ml iodine flask. Add 75 ml reagent water and 0.5 g of  $\text{KI}$  crystals. After solution is complete, add 10 ml of 1:4  $\text{H}_2\text{SO}_4$ . Stopper and let stand 5 minutes in the dark. Titrate with the  $\text{Na}_2\text{S}_2\text{O}_3$  solution being standardized using starch indicator. Calculate the normality of the sodium thiosulfate standard solution using the following equation:

$$N = \frac{0.25}{S}$$

Where  $N$  = normality,  $S$  = mls  $\text{Na}_2\text{S}_2\text{O}_3$  required for titration.

- p. Starch Indicator: Make a paste of 1 g soluble starch (iodometric) with cold water. Pour into 100 ml boiling water and boil for several minutes. Store in a cool place. The solution is stable for 2 to 3 days.

q. Sulfuric Acid, 1:4: Add 1 volume of conc.  $\text{H}_2\text{SO}_4$  to 4 volumes of reagent water.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Procedure

Soluble iron, manganese, and organic matter are removed by shaking approximately 400 ml of the sample with excess  $\text{CaO}$ . Filter, discarding the first 75 ml of filtrate.

### a. Iodide

(1) Measure 100 ml of the sample or an aliquot containing less than 5 mg iodide into a 250 ml iodine flask. Dilute to 100 ml with reagent water if necessary. Add 1 drop of methyl red indicator. Make slightly acidic with 1:4  $\text{H}_2\text{SO}_4$ . Add 15 ml sodium acetate solution and 5 ml acetic acid (1:8). Add bromine water until a light yellow color is produced. Mix and allow to stand 5 minutes.

(2) Add sodium formate solution until the yellow color disappears; then add 1 ml excess. Wash down the sides of the flask with a small amount of reagent water. Insert a syringe and glass tube in the flask and blow out the bromine vapors. If iron precipitates, add 0.5 g  $\text{KF} \cdot 2\text{H}_2\text{O}$ .

(3) Dissolve 1 g  $\text{KI}$  in the sample and add 10 ml  $\text{H}_2\text{SO}_4$  (1:4). Let the flask stand 5 minutes in the dark. Titrate the liberated iodine with the standard sodium thiosulfate solution to a light yellow. Add 2 - 3 ml starch indicator and continue titrating to the starch end point. After the end point has been reached, disregard the return to blue color.

### b. Bromide and Iodide

(1) Measure 100 ml of the sample or an aliquot containing less than 5 mg bromide into a 250 ml iodine flask. (See Note 1.) Dilute to 100 ml with reagent water if necessary. Add  $\text{NaCl}$  until a concentration of 3 g chloride ion is reached. (Generally, with sea water approximately 2.5 g are required depending upon the chloride content already present.) Add 1 drop of methyl red indicator and neutralize the solution with  $\text{HCl}$  (1:4). Add 10 ml  $\text{KClO}$  solution, 1 ml  $\text{HCl}$  (1:4), and  $\text{CaCO}_3$  to an excess of 0.1 g. Heat to boiling for 8 minutes.

NOTE 1 - For high bromide concentrations, use a sample containing less than 25 mg bromide and titrate with 0.05N  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Prepare the 0.05N  $\text{Na}_2\text{S}_2\text{O}_3$  solution by diluting 500 ml of the stock solution to 1 liter with reagent water.

(2) To reduce the excess  $KClO_3$ , add 2 ml sodium formate solution. Wash down the sides of the flask with a small amount of hot, reagent water. Keep the solution hot for an additional 8 minutes and then cool. Add several drops of sodium molybdate solution. If iron precipitates, add 0.5 g  $KF \cdot 2H_2O$ .

(3) Treat and titrate the sample as outlined in paragraph a(3).

#### 10. Calculations

$$\text{ppm Iodide} = \frac{21,150 \times AN_1}{SD}$$

$$\text{ppm Bromide} = 13,320 \times \frac{(BN_2 - AN_1)}{TD} \quad \frac{SD}{SD}$$

Where,

A = ml sodium thiosulfate required for iodide titration

B = ml sodium thiosulfate required for bromide titration

D = specific gravity of sample

$N_1$  = normality of sodium thiosulfate solution used in iodide titration

$N_2$  = normality of sodium thiosulfate solution used in bromide titration

S = ml sample for iodide determination

T = ml sample for bromide determination

#### 11. Precision and Accuracy

Precision and accuracy vary with the volume of sample used - greater volume yields greater precision and accuracy.

### SECTION 7. CALCIUM AND MAGNESIUM IN SEA WATER

#### 1. Scope and Application

This method outlines the procedure for determining calcium and magnesium in sea water. The method is applicable to sea water and product water.

#### 2. Principle of Method

Calcium and magnesium are determined in sea water by titrating with EDTA (ethylenediamine tetraacetic acid or its salt). The calcium will combine with EDTA first and is determined at a pH which is sufficiently high to precipitate

magnesium as the hydroxide. An indicator which is specific for calcium is used. A second sample is titrated at a lower pH which allows the magnesium to remain in solution. Total calcium and magnesium are determined on this sample. The magnesium content is calculated from the ml titrant used for the first sample and total used for the second sample.

### 3. Interferences

Interferences which may be present in sea water samples are Cu, >2 mg/l;  $\text{Fe}^{+2}$ , >20 mg/l;  $\text{Fe}^{+3}$ , >20 mg/l; Mn, 10 mg/l; Zn, 5 mg/l; Pb, 5 mg/l; Al, 5 mg/l; Sn, 5 mg/l. These interferences are removed in this procedure.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

- a. Miscellaneous Glassware - burets, pipets, erlenmeyer flasks.
- b. Filter Paper - Whatman #1 and #42.

### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

### 7. Reagents

- a. Thioacetamide, 1M: Dissolve 7.5 g  $\text{CH}_3\text{CSNH}_2$  in 100 ml reagent water.
- b. Ammonium Hydroxide, 6N: Dilute 400 ml conc.  $\text{NH}_4\text{OH}$  to 1 liter with reagent water.
- c. Sodium Hydroxide, 1N: Dissolve 40 g NaOH in 1 liter reagent water.
- d. Calvert II Indicator: Available commercially.
- e. EDTA Titrant, 0.01M: Dissolve 3.723 g of disodium ethylenediamine tetraacetate dihydrate in reagent water and dilute to 1 liter. Standardize against standard calcium solution. Adjust to 1 ml = 1 mg  $\text{CaCO}_3$ .
- f. Buffer Solution: Dissolve 16.9 g  $\text{NH}_4\text{Cl}$  in 143 ml conc.  $\text{NH}_4\text{OH}$ . Add 1.25 g EDTA magnesium salt (tetraacetic acid magnesium disodium salt) and dilute to 250 ml with reagent water.

g. Eriochrome Black T Indicator: Dissolve 0.5 g dye and 4.5 g hydroxylamine hydrochloride in 100 ml 95% ethyl alcohol.

h. Standard Calcium Solution: Weigh 1.0000 g anhydrous calcium carbonate into a 500 ml erlenmeyer flask. Add 1:1 HCl dropwise until the  $\text{CaCO}_3$  has dissolved. Add approximately 200 ml reagent water and boil 5 minutes. Cool and add 3 drops methyl red indicator. Adjust the pH by adding either 6N  $\text{NH}_4\text{OH}$  or 1:1 HCl as required until the solution color is orange. Transfer to a 1 liter volumetric flask and dilute to the mark with reagent water. One (1) ml of this solution is equivalent to 1 mg  $\text{CaCO}_3$ .

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Procedure

### a. Calcium

Dilute 5 ml of the sea water sample to 10 ml with reagent water. Add 1 ml of 1M thioacetamide solution and heat without boiling. Cool and filter through a #42 Whatman filter paper. Make alkaline with 6N  $\text{NH}_4\text{OH}$  and heat without boiling. Cool and filter through a #1 Whatman filter paper. Add 1N NaOH to a pH greater than 12. Dilute to 50 ml with reagent water. Add 1 scope (scope furnished with indicator) Calvert II indicator and titrate with 0.01M EDTA. The color change at the end point is red to blue.

### b. Magnesium and Calcium

Dilute 5 ml of the sea water sample to 10 ml with reagent water. Add 1 ml of 1M thioacetamide solution and heat without boiling. Cool and filter through a #42 Whatman filter paper. Add buffer solution dropwise to pH 10 and heat without boiling. Cool and filter through a #1 Whatman filter paper. Dilute to 50 ml with reagent water. Add 1/2 ml Eriochrome Black T indicator and titrate with 0.01M EDTA to the blue end point.

## 10. Calculations

### a. Calcium

$$\text{mg/l (ppm) Ca} = \frac{\text{ml EDTA} \times 400.4 \times f}{\text{ml sample}}$$

$$f = \frac{\text{mg CaCO}_3}{\text{ml EDTA}}, \text{ where 0.01M EDTA is used, } f = 1$$

b. Magnesium

$$\text{mg/l (ppm) Mg} = \frac{\text{ml EDTA (Mg + Ca)} - \text{ml EDTA (Ca)} \times 243}{\text{ml sample}}$$

11. Precision and Accuracy

Precision and accuracy are governed by sample size and buret graduations.

## SECTION 8. CARBON DIOXIDE (TOTAL) IN SEA WATER

1. Scope and Application

This method covers the determination of total carbon dioxide, both dissolved and chemically combined, in sea water. The method is applicable to sea water, deaerated sea water, and product water.

2. Principle of Method

Upon acidifying and heating, carbon dioxide is liberated from the sample in a closed system. The carbon dioxide is passed through a solution of barium hydroxide with which it combines, and the excess hydroxide is titrated with standard acid.

3. Interferences

No interferences have been found when analyzing sea water.

4. Definitions

Definitions of terms used are given in this report Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

5. Apparatus

a. Burets - 2, 50 ml

b. Double Friedrichs Condenser - similar to Scientific Glass Apparatus Co., Inc. catalog # C-7810.

c. Circulating Pump - fully closed, bellows or diaphragm type, capable of circulating at least 1 liter of air per minute against the static water head of the system.

d. Expansion Bladder - 2 inch diameter Gooch crucible tubing, 30 inch for 1 liter flask, 2-30 inch for 3 liter flask.

- e. Heat Barrier - 1 inch thick asbestos board, 12 x 12 inches.
- f. Evolution Flasks - 3 liters and 1 liter, 3-neck distillation flasks.
- g. Absorption Flask - 3 x 30 cm tube.
- h. Ring Support.
- i. Dry Trap - Fleming purifying jar, 38 x 190 mm.
- j. Rubber Bands for securing bladder.
- k. Hot Plate.
- l. Mist Trap - calcium chloride tube filled with glass wool.
- m. Stopcocks - 6 mm tubing size.
- n. Sample Inlet - 12 mm glass tube.
- o. Evacuation Tube - 12 mm glass tube.
- p. Pinch Clamps.
- q. Carbon Dioxide Trap - 250 ml separatory funnel filled with Ascarite.
- r. Tygon Tubing - for connections.
- s. Sample Vessels - 200, 500, and 1,000 ml sized (see description under paragraph 8 below).

## 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water." In addition, for this analysis, reagent water shall mean carbon dioxide-free water.

## 7. Reagents

a. Sulfuric Acid, conc.: Use as scrubbing solution.

b. Sulfuric Acid, 1M: Add 98 g conc.  $\text{H}_2\text{SO}_4$  to reagent water and dilute to 1 liter.

c. Hydrochloric Acid, 0.04N: Dilute 3.42 ml conc.  $\text{HCl}$  to 1 liter with reagent water and standardize.

d. Barium Hydroxide Solution: Dissolve 5.0 g  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  in 1 liter reagent water. Store in a bottle fitted with an automatic-zero buret. Protect

air inlets for the bottle and buret with drying tubes filled with Ascarite. Barium chloride (2.7 g) may be added to reduce the solubility of barium carbonate.

e. Phenolphthalein Indicator Solution: Dissolve 1 g phenolphthalein in a mixture of 100 ml reagent water and 100 ml ethyl alcohol.

## 8. Sampling

Samples shall be taken in previously cleaned glass vessels. Dual samples shall be taken for each analysis. Sample vessels shall be of 200, 500, and 1,000-ml sized depending upon the  $\text{CO}_2$  concentration - lower  $\text{CO}_2$  concentration will require larger sample. Sample vessels shall be similar to Scientific Glass Apparatus Co., Inc. catalog #G-2595. Samples shall be taken with dual sampling vessels in the vertical position, inlet at bottom and outlet at top. Vessels shall be allowed to purge for 5 minutes. Stopcocks are closed simultaneously after purging.

## 9. Procedure

Assemble apparatus as shown in Figure 2. Mounting on a stand or plywood frame provides the apparatus with stability and mobility.

### a. Blank Determination

Acidify 400 ml of distilled water to approximately pH 4 with 1M  $\text{H}_2\text{SO}_4$ . Boil vigorously for 15 minutes in an erlenmeyer flask to expel  $\text{CO}_2$ . Place 50 ml  $\text{Ba}(\text{OH})_2$  solution and 5 drops phenolphthalein indicator in the absorption flask and secure on stopper as shown in Figure 2. Add 200 ml of the freshly boiled water to the evolution flask (see Note 1). Isolate the evolution flask and condenser from the rest of the apparatus by manipulating stopcocks. Pull a vacuum on this part of the system through the evacuation tube. Build the pressure back to atmospheric by letting air in through the Ascarite-filled separatory funnel. By manipulation of stopcocks connect the evolution flask and condenser to the rest of the system.

Acidify the sample with 15 ml of 1M  $\text{H}_2\text{SO}_4$  and heat to boiling with a hot plate. After boiling has begun, circulate the evolved gas through the system with the circulating pump (see Note 2). Circulate for 10 minutes and then, while continuing circulation, titrate the excess barium hydroxide with 0.04N HCl to the phenolphthalein end point. Record the ml HCl required as "A."

### b. Sample Determination

Clean the apparatus thoroughly prior to each analysis. The sample size used will depend on the amount of  $\text{CO}_2$  present. Samples of 200 ml have been found satisfactory when the  $\text{CO}_2$  content is in the 1 to 50 ppm range. Larger samples, 500 or 1,000 ml, are necessary if the  $\text{CO}_2$  content is below 1 ppm. Sample size may be determined by weighing the sample vessel before and after introduction into the evolution flask or by using a vessel of known volume. By

manipulation of stopcocks, isolate the condenser and evolution flask from the rest of the system. Pull a vacuum on this part of the system through the evacuation tube. Close off the inlet with a pinch clamp then insert the sample vessel. Open the stopcock on the vessel nearest the inlet and allow the sample to flow into the evolution flask by releasing the pinch clamp. Close the pinch clamp and add 15 ml 1M H<sub>2</sub>SO<sub>4</sub>. Bring the pressure back to atmospheric by letting air in through the Ascarite-filled separatory funnel. By manipulation of stopcocks connect the evolution flask and condenser to the rest of the system. Heat to boiling and then circulate the evolved gas for 10 minutes. While continuing circulation, titrate the excess barium hydroxide with 0.04N HCl to the phenolphthalein end point. Record the ml HCl required as "B."

NOTE 1 - Glass beads may be added to prevent bumping.

NOTE 2 - Start and stop the pump several times to prevent priming.

#### 10. Calculations

Total carbon dioxide, ppm = 110N (A-B)

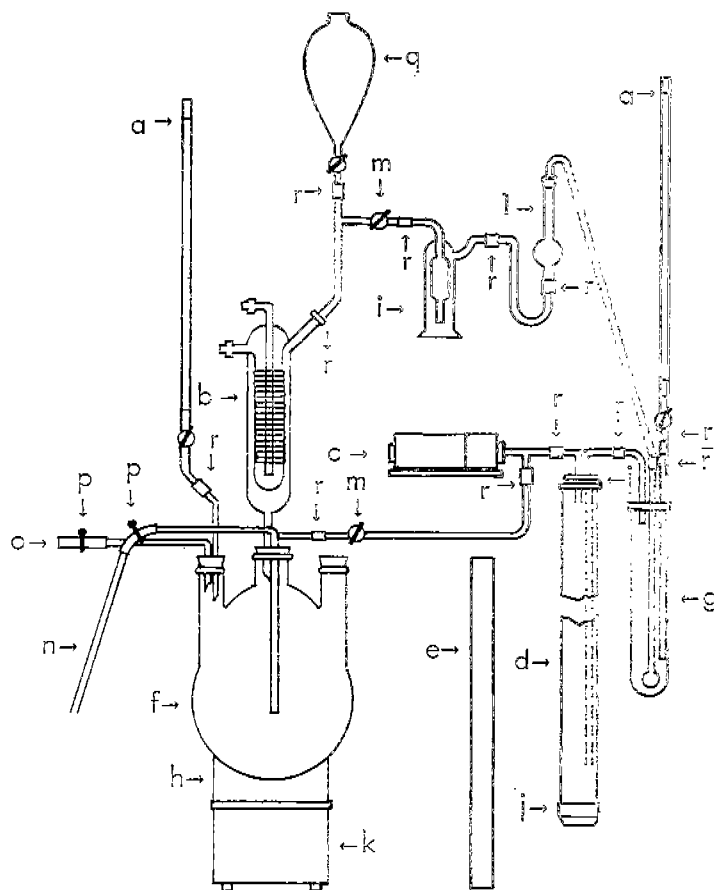
where, N = normality of HCl

A = ml HCl for blank titration

B = ml HCl for sample titration

#### 11. Precision and Accuracy

Results are accurate and reproducible to 0.2 ppm CO<sub>2</sub> for low CO<sub>2</sub> concentrations (1 to 5 ppm).



- a. Burets
- b. Double Friedrichs Con-  
denser
- c. Circulating Pump
- d. Expansion Bladder
- e. Heat Barrier
- f. Evolution Flasks
- g. Absorption Flask
- h. Ring Support
- i. Dry Trap
- j. Rubber Bands for  
securing bladder
- k. Hot Plate
- l. Mist Trap
- m. Stopcocks
- n. Sample Inlet
- o. Evacuation Tube
- p. Pinch Clamps
- q. Carbon Dioxide Trap
- r. Tygon Tubing

Figure 2

## SECTION 9. CHLORINE (RESIDUAL) IN SEA WATER

### 1. Scope and Application

This method outlines the procedure for determining residual chlorine in sea water. The method is applicable to sea water and product water.

### 2. Principle of Method

Orthotolidine in the presence of chlorine yields a yellow color. The intensity of the color increases with increasing chlorine concentration. In this method, the color developed in the sample is compared with chlorine standards. Commercially available color comparators are recommended for simplicity. Approximately 0.1 mg/l is detectable with this method.

### 3. Interferences

Turbidity will interfere and if high, it should be removed by centrifuging prior to the test. Other interferences are not normally present in sea water.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

Color comparator and standards - available commercially from Hach Chemical Company, Hall, Taylor or scientific supply houses.

### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

### 7. Reagents

Orthotolidine Reagent: Available commercially or prepared by dissolving 1.35 g orthotolidine dihydrochloride in 500 ml reagent water. Add this solution, with stirring, to a mixture of 350 ml reagent water and 150 ml conc. HCl. Store in an amber, screw-cap bottle. Do not use a rubber stopper. The solution is not stable for more than 6 months.

### 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

### 9. Procedure

Place an aliquot of the sample in the sample cell provided with the comparator. Add 0.5 ml orthotolidine reagent and mix. Untreated aliquots of the sample are added to the other sample cells (may be one or two cells depending on comparator purchased) for comparison. The color of the sample is compared with the standards within 5 minutes of treatment.

### 10. Calculations

No calculations are required. The mg/l chlorine is arrived at by comparison with standards.

## SECTION 10. CHLOROSITY OF SEA WATER

### A. Mercuric Nitrate Method

#### 1. Scope and Application

This method covers the titrimetric determination of the chlorosity of sea water. The chlorosity is expressed as grams per liter chlorides. The method is applicable to analysis of sea water, boiler water, and product water. In boiler waters where low chloride concentrations must be determined accurately, it is particularly useful.

#### 2. Principle of Method

Chlorosity is determined by titrating with mercuric nitrate using diphenylcarbazone as the end point indicator. Soluble mercuric chloride is formed. The pH of the sample is adjusted to 2.3 - 2.8 with nitric acid. In this range the indicator forms a purple complex with excess mercuric ions at the end point. A more accurate end point occurs at the change from greenish blue to blue; however, the analyst may find the purple end point easier to determine. Any error is corrected by titrating a blank of reagent water and using the same end point for the sample. Two methods of enhancing the end point are given. One is the use of xylene cyanol FF in the indicator solution. The other is the addition of methanol to the sample. For chlorosity determinations in sea water both methods should be used.

#### 3. Interferences

Interferences include bromide and iodide, which are titrated as chloride, and sulfite, chromate, and ferric ions. Sulfite, chromate, and ferric ions are not present in sufficient quantities to cause interferences in the analysis of sea water.

#### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

#### 5. Apparatus

- a. Buret, 50 ml (5 ml microburet may be used for greater accuracy)
- b. Magnetic stirrer and stirring bar (teflon coated) - not required
- c. 1 ml pipet
- d. 100 ml volumetric flasks

- e. 25 ml pipet
- f. 100 ml graduated cylinder
- g. 250 ml beakers

## 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

## 7. Reagents

Mercuric nitrate and indicator solutions must be stored in dark bottles. The indicator solution will deteriorate causing a slow end point and high results. Storage in a refrigerator slows the deterioration.

a. Indicator-acidifier Reagent: Dissolve 0.25 g diphenylcarbazone and 0.03 g xylene cyanol FF in a mixture of 4.0 ml conc. nitric acid and 100 ml 95% ethyl alcohol.

b. Methanol: Reagent grade.

c. Standard Mercuric Nitrate Solution, 0.0282N: Dissolve 5.0 g  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  in a 100 ml reagent water containing 0.5 ml conc.  $\text{HNO}_3$ . Dilute to 900 ml and standardize against the standard NaCl solution. Adjust mercuric nitrate solution to exactly 0.0282N and perform a final standardization. Standardization is accomplished by titrating 5 ml samples of the standard NaCl solution as outlined under Procedure. 1 ml of mercuric nitrate standard equals 1 mg Cl. For greater accuracy, 0.0141N mercuric nitrate may be prepared.

d. Standard Sodium Chloride Solution: Dissolve 1.6482 g of previously dried ( $105^\circ\text{C}$  for 2 hrs.) ACS grade NaCl in reagent water and dilute to 1 liter. This solution contains 1 mg Cl per 1 ml.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Procedure

Use a sample aliquot containing not more than 5 mg Cl in 25 ml. For sea water determination, pipet 1 ml of the sample into a 100 ml volumetric flask. Dilute to the mark with reagent water.

a. To a 25 ml aliquot (see Note 1) of the diluted sample, add 0.5 ml of the indicator-acidifier reagent. A greenish-blue color should be observed at this point. If the color is green or blue, a preliminary pH adjustment of the sample to pH 8.0 will be necessary before addition of the indicator acidifier reagent.

b. Add 25 ml of methanol (see Note 2) and titrate using the standard mercuric nitrate solution to the light blue end point (or purple end point if preferred). See Note 3.

c. Perform a blank determination by titrating 25 ml reagent water and 25 ml methanol.

NOTE 1 - Greater accuracy can be obtained by titrating the entire 100 ml.

NOTE 2 - A 3 to 1 ratio of methanol to sample was found to provide the most satisfactory color change at the end point. However, a 1 to 1 ratio is satisfactory in sea water determinations.

NOTE 3 - The color change used for end point determination depends upon the analyst. However, the same color change must be used for the blank and sample.

For product water, an undiluted sample should be analyzed as outlined above.

## 10. Calculations

### a. Sea Water

$$\text{Chlorosity, g/l} = \frac{A - B \times N \times 35.453 \times 4}{\text{ml sample (for sea water, = 1)}}$$

Where,

A = ml standard mercuric nitrate required for sample

B = ml standard mercuric nitrate required for blank

N = normality of standard mercuric nitrate

If the mercuric nitrate standard is exactly 0.028N (1 ml = 1 mg Cl) and a 25 ml aliquot of the diluted sample is used, the following equation applies:

$$\text{Chlorosity, g/l} = 4(A - B)$$

Where,

A = ml standard mercuric nitrate required for the sample

B = ml standard mercuric nitrate required for the blank

## b. Product Water

$$\text{Chlorosity, g/l} = \frac{A - B \times N \times 35.453}{\text{ml sample}}$$

A = ml standard mercuric nitrate required for sample

B = ml standard mercuric nitrate required for blank

N = normality of standard mercuric nitrate

To calculate the ppm chlorides, multiply either of the above equations by 1,000.

## 11. Precision and Accuracy

The individual analyst can reproduce his results within 50 ppm or 0.05 grams per liter when analyzing sea water.

# SECTION 11. CHLOROSITY OF SEA WATER

## B. Silver Nitrate Method

### 1. Scope and Application

This method covers the determination of sea water chlorosity. The method is applicable to the analysis of sea water and product water.

### 2. Principle of Method

Silver nitrate when added to a neutral or slightly alkaline solution containing chlorides will quantitatively precipitate the chlorides as silver chloride. Potassium chromate is used as the end point indicator. The end point change is yellow to the first appearance of red.

### 3. Interferences

Interferences which are present in sea water include bromides and iodides. Bromide and iodide ions are precipitated by silver nitrate and register as equivalent chloride. This method does not provide a way of eliminating these interferences. However, when determining chlorosity in sea water, bromide and iodide interferences are negligible due to the comparatively high chloride concentration and the reproducibility of the method.

#### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

#### 5. Apparatus

- a. 250 ml erlenmeyer flasks
- b. Buret (any size, smaller graduations increase accuracy)
- c. 1 ml pipet
- d. 100 ml graduated cylinder

#### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

#### 7. Reagents

a. Potassium Chromate Indicator: Dissolve 50 g  $K_2CrO_4$  in 100 ml reagent water. Add silver nitrate solution until a definite red precipitate is formed. Allow to stand 12 hours, then filter and dilute the filtrate to 1 liter with reagent water.

b. Standard Silver Nitrate Solution, 0.0282N: Dissolve 4.7920 g  $AgNO_3$  in reagent water and dilute to 1 liter. Standardize against 0.0282N NaCl solution. (See Procedure.) Adjust the  $AgNO_3$  solution until it is exactly 0.0282N. 1 ml of this solution is equivalent to 1 mg Cl. (KEEP IN A DARK BOTTLE. Light causes decomposition.)

c. Standard Sodium Chloride Solution, 0.0282N: Dissolve 1.6482 g of predried reagent grade NaCl in reagent water and dilute to 1 liter. 1 ml of this solution contains 1 mg Cl.

#### 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Procedure

### a. Standardization of Silver Nitrate Solution

Pipet 10 ml 0.0282N NaCl into an erlenmeyer flask containing 100 ml reagent water. Add 1 ml  $K_2CrO_4$  indicator solution. Using a buret, titrate the NaCl standard with  $AgNO_3$  solution to a pinkish-yellow end point. (See Note 1.) Titrate a blank of 100 ml reagent water in the same manner. Calculate the normality of the  $AgNO_3$  solution using the following equation:

$$ml\ NaCl \times Normality\ NaCl = ml\ AgNO_3\ sample - ml\ AgNO_3\ blank \times N\ AgNO_3$$

Adjust the  $AgNO_3$  solution to exactly 0.0282N if necessary.

NOTE 1 - Some analysts prefer titrating to a reddish-yellow end point. The accuracy of the method depends on the analyst's consistency in selecting end points.

### b. Sea Water Determination

Pipet 1 ml of the sea water sample into an erlenmeyer flask containing 100 ml reagent water. (See Note 2.) Add 1 ml  $K_2CrO_4$  indicator solution. Titrate with 0.0282N  $AgNO_3$  to a pinkish-yellow end point. Treat a blank of 100 ml reagent water in the same manner. Record the ml  $AgNO_3$  required for the sample and the blank.

NOTE 2 - For greater accuracy, a blank should be determined for each analysis. The end point selected for the sample should be as close as possible to the blank end point.

## 10. Calculations

$$mg/l\ Cl = \frac{(ml\ AgNO_3\ sample - ml\ AgNO_3\ blank) \times N\ AgNO_3 \times 35,460}{ml\ sample}$$

$$Chlorosity = \frac{mg/l\ Cl}{1,000}$$

## 11. Precision and Accuracy

The accuracy of the method depends on the analyst's consistency in selecting end points. Generally, results can be reproduced within 100 ppm or 0.1 grams per liter when analyzing sea water.

## SECTION 12. COLIFORM DETECTION IN SEA WATER

### 1. Scope and Application

This method outlines the procedure for coliform detection in sea water using the membrane filter technique. The method is applicable to sea water and product water.

### 2. Principle of Method

The membrane filter technique for detecting coliform group bacteria consists of three steps - filtration, incubation, and counting. The incubation period is reduced to 20 hours compared to 24-48 hours using other methods. Overall, the membrane filter technique provides a direct count as opposed to a statistical estimate in one-fourth the time.

Colonies formed from coliform bacteria exhibit a characteristic golden, metallic sheen in the presence of a differential type nutrient medium. Each colony results from a single organism, and analytical results are reported as the number of coliform organisms per 100 ml of sample. The United States Public Health Service has specified that the standard sample shall consist of not less than 50 ml and that the arithmetic mean coliform density of all standard samples per month shall not exceed one per 100 ml. Limits specified per standard sample are 3/50 ml, 4/100 ml, or 13/500 ml in:

- a. Two consecutive samples.
- b. More than one standard sample when less than 20 are examined per month.
- c. More than five percent of the standard samples when 20 or more are examined per month.

These limits are for potable water.

### 3. Interferences

Interferences include turbidity which may cause plugging of the filter, a high density of noncoliform organisms which may cause low estimates when compared with MPN estimates, and the presence of heavy-metal ions, toxic substances, or high natural temperatures. When determining coliform count of finished water, these interferences are not normally present. In sea water, turbidity is the most likely source of interference. Other interferences may be present if sea water intakes are near sources of pollution such as industrial and human waste effluents.

#### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

#### 5. Apparatus

- |                                     |   |
|-------------------------------------|---|
| a. Sample bottles                   | - Pyrex, ground glass stoppered with wide mouth, 125 ml capacity.   |
| b. Dilution bottles                 | - Pyrex, ground glass stoppered or screw cap with graduation levels marked.   |
| c. Pipets and graduated cylinders   | - Any convenient size.  |
| d. Culture dishes                   | - 5 to 6 cm diameter, glass or plastic, Petri type.   |
| e. Filtration unit                  | - Filter holder similar to Millipore Catalog Numbers XX 20 047 20 or XX 10 047 00, Pyrex 1,000 ml filter flask, and vacuum pump.  |
| f. Membrane filters                 | - White grid, 47 mm diameter, 0.45 micron pore diameter, similar to Millipore Catalog Number HA WG 047 AO.  |
| g. Absorbent pads                   | - Included with filters.  |
| h. Magnifier for counting colonies  | - Similar to Millipore Catalog Number XX 62 000 08.   |
| i. Incubator                        | - Suitable for maintaining $35^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ with constant saturated humidity and air circulation.   |
| j. Sterilizer                       | - Autoclave with sufficient size to prevent crowding. The unit should be constructed to maintain uniform temperatures up to and including $121^{\circ}\text{C}$ . Pressure gauges and safety valves are required. |
| k. Forceps                          | - Stainless steel, similar to Millipore Catalog Number XX 62 000 06.  |
| l. Wrapping paper for sterilization | - Kraft, best quality sulfate pulp.   |

## 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

## 7. Reagents

a. Buffered Dilution Water: Prepare by dissolving 34.0 g potassium phosphate, monobasic,  $\text{KH}_2\text{PO}_4$ , in 500 ml reagent water. Adjust the pH to 7.2 with 1N NaOH and dilute to 1 liter with reagent water. Add 1.25 ml of this solution to 1 liter reagent water. Autoclave the desired amount for 20 minutes prior to use.

b. Endo Broth, MF: Dehydrated form available from scientific supply houses. Difco or BBL brand recommended.

c. Medium: Prepare as directed on manufacturer's label. Add 2% ethyl alcohol (95%) to the reagent water before adding the dehydrated medium. Heat and stir the medium until the boiling point is reached. Do not under boil or over boil. Pour the medium into a sterile, screw cap bottle and store in a refrigerator for not more than three days. Medium already prepared in glass vials containing 2 ml may be purchased if desired.

d. Malachite Green, negative stain, 0.01% solution: Dissolve 0.05 g malachite green in 500 ml reagent water.

e. Tetrazolium Chloride, positive stain, 2% solution: Dissolve 10 g 2, 3, 5 - triphenyl - tetrazolium chloride in 500 ml reagent water.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis. In addition, samples shall be taken in bottles which have been sterilized as outlined under Procedure. Care shall be taken when sampling not to contaminate the bottle or cap by hands. Do not place the sample line in the bottle. Do not rinse bottle with sample. Do not completely fill bottle. Leave at least 1 inch of air space to allow mixing prior to analysis.

## 9. Procedure

### a. Sterilization

(1) Filters and absorbent pads - Sterilize as received in paper envelopes for 10 minutes at  $121^\circ\text{C}$ .

(2) Filter holder - Wrap the funnel and base in Kraft paper and autoclave for 10 minutes at 121°C. Normally sterilization of the filter holder is not required between samples.

(3) Bottles - After thoroughly cleaning and drying, the bottles are autoclaved with cap or stopper in place for 30 minutes at 121°C or heated for 1 hour at 170°C.

(4) Pipets - After thoroughly cleaning and drying, wrap the pipets in Kraft paper or place in a cylindrical or rectangular, stainless steel or aluminum container. Autoclave for 30 minutes at 121°C or heat for 1 hour at 170°C.

(5) Graduated Cylinders - After thoroughly cleaning and drying, cover the mouth with aluminum foil and autoclave for 30 minutes at 121°C or heat for 1 hour at 170°C.

(6) Petri Dishes - Glass dishes should be thoroughly cleaned and dried. The dishes are placed in a metal container or wrapped in Kraft paper and autoclaved for 30 minutes at 121°C. Plastic disposable dishes may be purchased already sterilized. To reuse plastic dishes, sterilization may be accomplished by soaking in 70% ethyl alcohol over night and inverting on a sterile cloth to dry. Ultraviolet radiation may also be used.

(7) Forceps - Dip tips in 95% ethyl alcohol and ignite over flame.

b. Filtration (See Note 1)

Insert the filter holder base into a one liter vacuum flask which is connected to a suitable vacuum system (pump or water aspirator). Using the forceps, place a sterile membrane filter, grid side up, on the filter holder. Lock the funnel in place. Turn on the vacuum system and draw a sample of appropriate size (preferably 100 ml but at least 50 ml) through the filter (see Note 2). Rinse the funnel walls with three 20 ml portions of sterile buffered dilution water. Remove the filter from the holder with forceps and gently roll it onto the surface of an absorbent pad containing the medium (see Note 3). CAUTION: Avoid trapping air bubbles between the filter and absorbent pad. Replace the Petri dish cover immediately.

NOTE 1 - All equipment and reagents listed must be sterilized prior to use.

NOTE 2 - Mix sample in bottle by shaking prior to filtering.

NOTE 3 - Prepare Petri dishes for incubation by placing an absorbent pad in the dish and adding 1.8 to 2.2 ml of the medium. Replace dish cover until needed.

c. Incubation and Counting

The Petri dishes are incubated (see Note 4) in an inverted position for 20 - 22 hours at 35°C ± 0.5°C. After incubation remove the filter from the dish

and dry for 1 hour on absorbent paper. Count the colonies which have a metallic luster. Counts are made with the aid of a magnifier and a light source. Stains such as malachite green or tetrazolium chloride may be used to enhance visual contrast (see Note 5).

NOTE 4 - Incubation in constant, saturated humidity is required.

NOTE 5 - Flooding the filter with malachite green solution (0.01%) imparts a light green color to the filter area. Tetrazolium chloride solution (2%) imparts a red color to the colonies.

#### 10. Calculations

Coliform density of the sample is reported as number of colonies per 100 ml.

$$\text{Coliform colonies/100 ml} = \frac{\text{Coliform colonies counted} \times 100}{\text{ml sample filtered}}$$

### SECTION 13. COPPER IN SEA WATER

#### 1. Scope and Application

This method outlines the determination of copper in sea water. This method is applicable to sea water and product water.

#### 2. Principle of Method

Two (2) moles of 2,9-dimethyl - 1,10-phenanthroline (neocuproine) will react with 1 mole of cuprous ion to form an orange complex. The complex is extracted with a chloroform-isopropyl alcohol mixture and the absorbance is read at 457 mμ. The color obeys Beer's Law in concentrations up to 0.2 mg Cu per 25 ml of solvent. A pH between 3 and 9 in the aqueous system allows full color development. The color is stable in the chloroform-isopropyl alcohol mixture for several days. The minimum detectable concentration using this procedure is 0.002 mg Cu.

#### 3. Interferences

In sea water, this method is essentially free of interference.

#### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

## 5. Apparatus

- a. Spectrophotometer - for use at 457 m $\mu$ .
- b. 250 ml separatory funnels.
- c. 25 ml volumetric flasks.

## 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

In addition, for this analysis reagent water shall mean distilled water which has been deionized or redistilled using glass apparatus to give copper-free water.

## 7. Reagents

a. Copper Stock Solution: Dissolve 0.2000 g of polished electrolytic copper wire in 10 ml of reagent water and 5 ml concentrated HNO<sub>3</sub>. After the reaction has slowed, warm gently to complete solution and then boil to expel nitrogen oxides. Cool and add 50 ml of reagent water. Transfer to a 1 liter volumetric flask and dilute to the mark with reagent water. This solution contains 0.200 mg Cu per ml.

b. Standard Copper Solution: Dilute 50 ml of the stock solution to 500 ml with reagent water. One (1) ml of this solution contains 0.02 mg Cu.

c. Hydroxylamine Hydrochloride Solution: Dissolve 50 g of NH<sub>2</sub>OH·HCl in 450 ml reagent water.

d. Nitric Acid, 1:9: Add 1 volume concentrated HNO<sub>3</sub> to 9 volumes reagent water. This mixture is used for cleaning glassware.

e. Sodium Citrate Solution: Dissolve 150 g Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O in 400 ml reagent water. Add 5 ml NH<sub>2</sub>OH·HCl solution, 10 ml neocuproine, and 50 ml chloroform. Discard the chloroform layer which contains any Cu impurities that may have been present.

f. Ammonium Hydroxide Solution, 6N: Dilute 400 ml concentrated ammonium hydroxide to 1 liter with reagent water and store in a polyethylene bottle.

g. Neocuproine Reagent: Dissolve 0.1 g of neocuproine in 100 ml methanol. Stability of this solution is at least 1 month.

h. Chloroform - reagent grade.

i. Isopropyl Alcohol - reagent grade.

j. pH Paper - range 4 - 6.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Sufficient concentrated HCl, plus 2 ml for each liter of sample to be taken, is added to the sample bottle prior to sampling to neutralize the sample to pH 4. This procedure eliminates the possibility of some copper plating on the walls of the container.

Samples shall be at room temperature prior to analysis.

## 9. Calibration and Standardization

Prepare a series of standards (0.002 to 0.10 mg Cu) using the standard copper solutions. Dilute to 100 ml with reagent water and develop the color as outlined under Procedure. Measure the absorbance and plot against mg Cu. If chloroform is used as reference, the absorbance values must be corrected by subtracting the absorbance of the reagent blank. For smaller amounts of copper, a calibration curve may be prepared by diluting 10 ml of the standard copper solutions to 100 ml and carrying 1 to 10 ml volumes through the described procedure. Use of a larger cell in the spectrophotometer will be required to increase sensitivity.

## 10. Procedure (See Note 1)

Pipet 100 ml of the sample or an aliquot containing 0.004 - 0.2 mg Cu, into a 250 ml separatory funnel. Dilute with reagent water if necessary. Add 5 ml hydroxylamine hydrochloride solution and 10 ml sodium citrate solution. Mix thoroughly and then adjust the pH to 4 - 6 with the 6N ammonium hydroxide or 1:9 nitric acid. (pH test paper showing a color change in the 4 - 6 range may be used as the indicator.)

Add 10 ml neocuproine reagent and 10 ml chloroform. The complex is extracted into the chloroform by stoppering the separatory funnel and shaking for 30 seconds. Allow the mixture to separate and then add the chloroform layer to a 25 ml volumetric flask. (See Note 2.) The extraction of the water layer is repeated using 10 ml chloroform. This extract is added to the previous one. Dilute the extracts to 25 ml using isopropyl alcohol. Stopper and mix thoroughly.

A portion of the solution is transferred to a suitable absorption cell, and the absorbance is measured at 457 m $\mu$  using a spectrophotometer. Chloroform or reagent water treated as the sample is used as a reference.

NOTE 1 - All glassware must be thoroughly cleaned. Soaking of sample bottles and other glassware in hot 1:9 HNO<sub>3</sub> for several hours is recommended.

NOTE 2 - Add approximately 5 ml isopropyl alcohol to each volumetric flask prior to addition of the extract.

### 11. Calculations

ppm Cu is determined by comparison of observed absorbance with the calibration curve and using the following equation:

$$\text{mg/l (ppm) Cu} = \frac{\text{mg Cu (from curve)} \times 1,000}{\text{ml aliquot}}$$

### 12. Precision and Accuracy

Precision and accuracy depend on the sample size and size of cell used with the spectrophotometer. Results can be reproduced to 0.002 mg Cu.

## SECTION 14. DISSOLVED OXYGEN IN SEA WATER

### A. Polarographic Method

#### 1. Scope and Application

This method outlines an instrumental procedure for determining dissolved oxygen in sea water. The method is applicable to sea water, deaerated sea water, and effluent.

#### 2. Principle of Method

Oxygen diffuses through a membrane and is electrically reduced at a cathode by applied voltage. This reaction causes a current to flow between the anode and cathode which is proportional to the partial pressure of oxygen in the sample. The signal is amplified and read directly on the meter or a 0-50 mv recorder.

#### 3. Interferences

No interferences have been found in sea water. If the sea water has been treated with chlorine, false readings will occur.

#### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

## 5. Apparatus

- a. Beckman Model 777 Laboratory Oxygen Analyzer
- b. Sample Bottles, BOD
- c. Magnetic Stirrer

## 6. Sampling

Samples shall be taken in previously cleaned, glass BOD bottles. Care shall be taken when sampling to exclude air bubbles. This can be accomplished by using tubing to introduce the sample at the bottom of the BOD bottle and purging for several minutes. If necessary, a cooling coil should be used to cool the sample to 15° to 45° C when the sample is taken. When in-line DO analyses are made, a tightly closed container with a thermometer and inlet and outlet shall be used. The inlet shall be at the bottom of the container with the outlet flush with the top to prevent trapping of air.

## 7. Procedure

### a. Calibration (See Note 1)

Prior to analysis the temperature and chlorosity of the sample must be determined. This should be done on a sample taken at the same time as the one on which the DO analysis will be made. After the temperature and chlorosity have been determined, use these results and the graph shown in Figure 3 to arrive at the calibration number. Zero the instrument and then switch to the proper range dial and wave the sensor in the air. Using the calibration dial, set the instrument to the calibration number.

### b. DO analysis (See Note 2)

After completing the calibration, insert the sensor in the sample bottle making sure that no air is trapped on the tip of the sensor or at the top of the bottle. Select the proper range setting and allow a few seconds for the instrument to stabilize. The meter reading on the scale corresponding to the range setting is in ppm DO.

NOTE 1 - When not in use store the tip of the sensor in distilled water. Carefully dry the tip before calibrating in air. The probe must be changed periodically due to fouling. Instructions and a kit for this are furnished with the instrument. (CAUTION: Extreme care shall be taken not to contaminate the sensor by touching the tip.)

NOTE 2 - Agitation of the sample is required during analysis. This can be accomplished by placing a stirring bar in the BOD bottle prior to taking the sample. The bottle can then be placed on a magnetic

stirrer for agitation when the analysis is made. When in-line analysis is made, agitation is provided by the flow of sample.

8. Calculations

No calculations are necessary. The meter reading is in ppm DO.

9. Precision and Accuracy

Results are accurate and reproducible to 25 ppb.

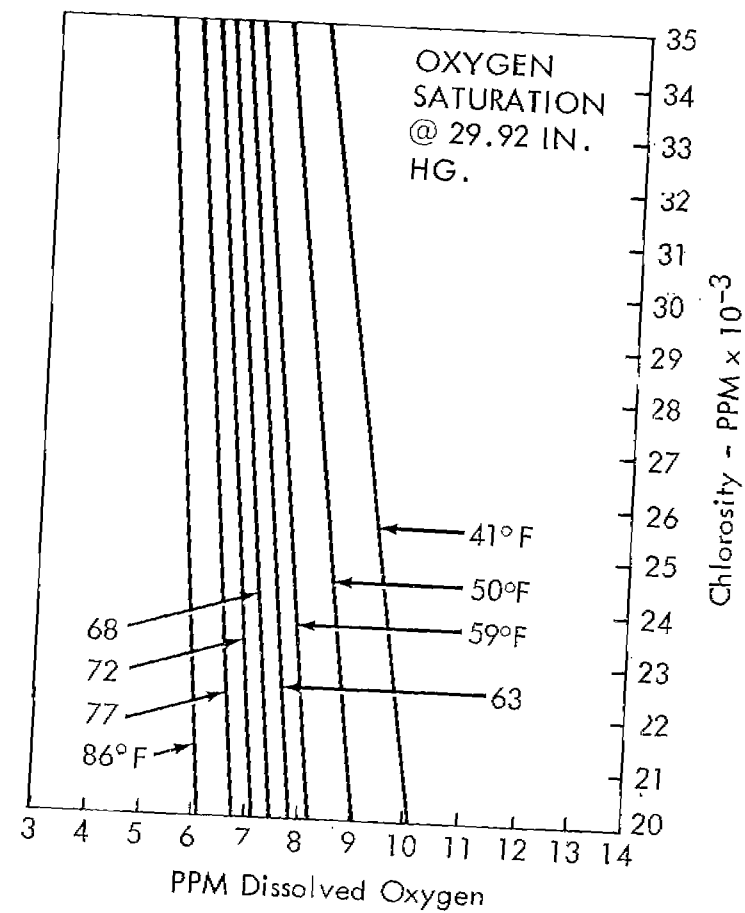
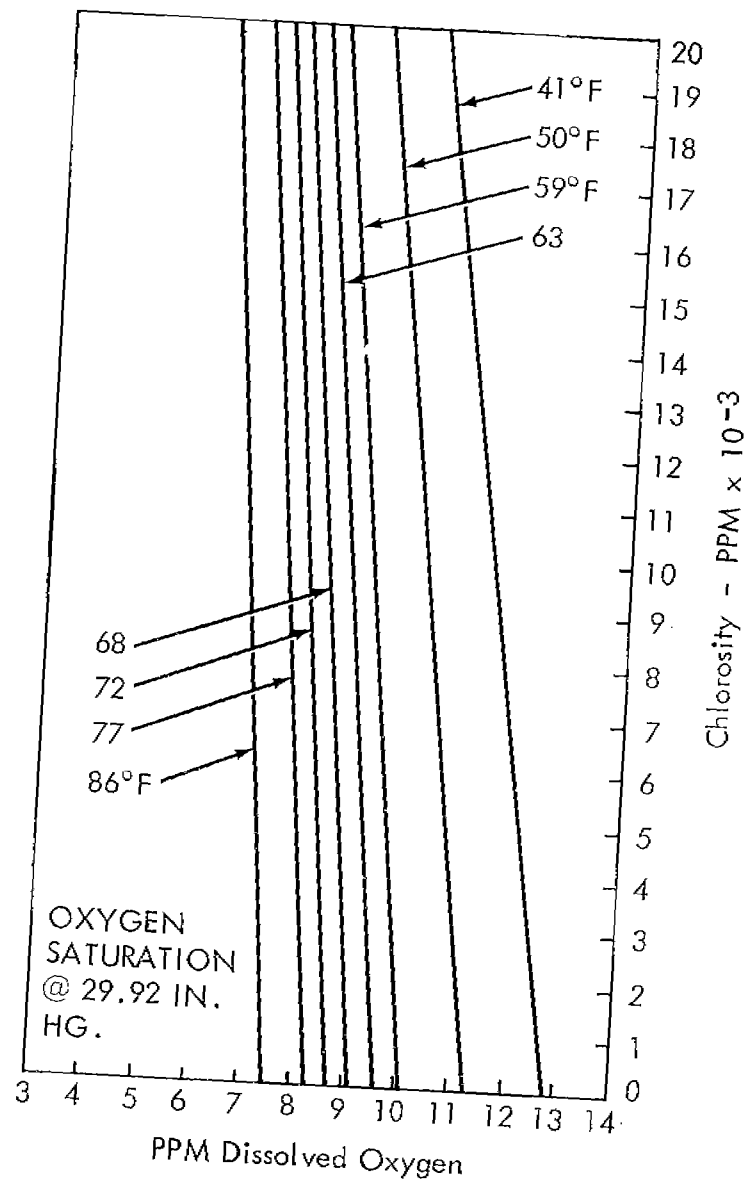


Figure 3

## SECTION 15. DISSOLVED OXYGEN IN SEA WATER

### B. Modified Winkler Method

#### 1. Scope and Application

This method outlines the determination of dissolved oxygen in sea water. The method is applicable to sea water; however, in deaerated sea water interferences may be present.

#### 2. Principle of Method

Free iodine is liberated in an amount equivalent to the oxygen in the sample. The iodine is titrated with a standard thiosulfate solution using starch indicator.

#### 3. Interferences

Interfering materials include ferrous and ferric iron. Their effects are negligible in sea water due to the low iron content and the comparatively high DO content. However, in deaerated sea water, where the DO content is in the 0-50 ppb range, the effects of ferrous and ferric iron become evident. The presence of one (1) ppm of ferrous iron results in an apparent loss of 0.14 ppm DO. The effect of up to 200 ppm ferric iron is eliminated in this method by the addition of potassium fluoride. Cuprous copper will also interfere if present. Other reducing or oxidizing materials are not normally present in sea water.

#### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

#### 5. Apparatus

- a. Microburet - 5 ml, 0.01 ml graduations.
- b. Sample Tube - 500 ml, specifications per ASTM Designation D888-49T, Figure 1.
- c. Sample Bottles - 300 ml capacity with tapered ground-glass stoppers.
- d. Pipets - 10 ml capacity, 0.1 ml graduations.

#### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

## 7. Reagents

a. Manganous Sulfate Solution: Dissolve 480 g  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  in reagent water, filter, and dilute to 1 liter.

b. Alkali - Iodide - Azide Reagent: Dissolve 500 g NaOH (or 700 g KOH) and 135 g NaI (or 150 g KI) in reagent water and dilute to 1 liter. Add 10 g  $\text{Na}_3\text{N}$  which has been dissolved in 40 ml reagent water to this solution.

c. Sulfuric Acid, conc.

d. Starch Solution: Make an emulsion of 5-6 g soluble starch with a small amount of reagent water. Pour into 1 liter of boiling, reagent water. Boil for a few minutes then allow to stand over night. Pour off the clear supernate and add 1.25 g salicylic acid for preservation.

e. Sodium Thiosulfate Stock Solution, 0.10N: Dissolve 24.82 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in boiled and cooled reagent water. Dilute to 1 liter. Add 5 ml chloroform to preserve the solution.

f. Standard Sodium Thiosulfate Solution, 0.025N: Dilute 250 ml sodium thiosulfate stock solution to 1 liter with boiled and cooled reagent water. Preserve by adding 5 ml chloroform. Standardize with potassium dichromate, 0.025N. One (1) ml is equivalent to 0.200 mg DO.

g. Standard Potassium Dichromate Solution, 0.025N: Dissolve 1.226 g of previously dried  $\text{K}_2\text{Cr}_2\text{O}_7$  ( $103^\circ\text{C}$  for 2 hrs.) in 1 liter reagent water.

Standardization - Dissolve 2 g KI in 100 ml reagent water. Add 10 ml 1:9  $\text{H}_2\text{SO}_4$  and 20 ml 0.025N potassium dichromate. Dilute to 200 ml and titrate to the starch end point with 0.025N sodium thiosulfate. When the solutions are of equal strength, 20 ml 0.025 sodium thiosulfate will be required. Adjust the strength of the thiosulfate solution to equal that of the dichromate solution.

h. Potassium Fluoride Solution: Dissolve 40 g  $\text{KF} \cdot 2\text{H}_2\text{O}$  in 1 liter reagent water.

## 8. Sampling

a. Sea Water

Take sample in 250 - 300 ml bottle. Place sampling tube at bottom of sample bottle. Purge for 5 minutes then slowly withdraw sample tube. Make sure no air bubbles are trapped in the sample bottle then seal the bottle with the ground glass stopper. Do not force the stopper but allow it to gradually settle into place. Samples may be fixed immediately by adding the manganous sulfate and alkali-iodide-azide solutions and conc.  $\text{H}_2\text{SO}_4$ . Titration may then be

delayed. If this is not practical the analysis of the sample should not be delayed more than 15 minutes. Methods of preservation for longer periods of time are not recommended.

b. Use sample tube described under paragraph 5b. Allow sample to flow through tube for 5 minutes at 400-500 ml per minute. The sample tube should be vertical with the inlet at the bottom and outlet at the top. Close off the top stopcock first and then immediately close the bottom one. Invert the tube and examine it to insure that no air bubbles have been trapped. Preferably, two (2) sample tubes should be used and connected by a Y so that simultaneous samples can be taken. On deaerated water, a cooling coil may be required to lower the sample temperature to 16 to 18°C. (NOTE - Sampling procedure is described further in ASTM Designation: D888-49T.) Samples may be fixed as described above or titrated immediately.

## 9. Procedure

### a. Sea Water

Add 2 ml manganous sulfate solution followed by 2 ml alkali-iodide-azide solution. (NOTE - add all solutions well below surface of sample.) Stopper the sample bottle making sure not to trap air bubbles. Mix by inverting the bottle several times. When the precipitate settles mix again and allow to settle. A ten-minute contact period is required. (See Note 1.) Remove stopper and immediately add 2 ml conc.  $\text{H}_2\text{SO}_4$  by allowing it to run down the neck of the bottle. Restopper and mix by inverting until all the precipitate has dissolved.

Titrate 203 ml with 0.025N sodium thiosulfate to a pale-yellow. Add 1-2 ml starch solution and continue titrating to the first disappearance of the blue color.

NOTE 1 - If the presence of ferric iron is suspected, add 1 ml KF solution prior to acidification.

### b. Deaerated Sea Water

Holding the sample tube vertically, add 2 ml alkali-iodide-azide solution to the upper nipple. (NOTE - Sample tubes as described in ASTM Designation: D888-49T have 2 ml calibration on the nipples.) Open the bottom stopcock then introduce the solution by slowly opening the top stopcock. (See Note 2.) Close the top stopcock when the 2 ml calibration mark is reached then close the bottom stopcock. (See Note 3.) Rinse both nipples with distilled water then flick out the excess and invert the tube. Fill the top nipple with 2 ml manganous sulfate solution and introduce as described for the alkali-iodide-azide solution. Rinse both nipples and mix by inverting. Allow a ten-minute contact period then add 2 ml conc.  $\text{H}_2\text{SO}_4$  as described for the other solutions. (See Note 3.) Mix by inverting until the precipitate has dissolved.

Titrate with 0.025N sodium thiosulfate (see Note 4) as described above under paragraph a except add 1-2 ml starch solution prior to beginning the titration. The second sample tube may be analyzed as a check.

NOTE 2 - The upper nipple is used for the addition of the alkali-iodide-azide solution. The lower nipples are for the addition of manganous sulfate solution and  $H_2SO_4$ .

NOTE 3 - The same point on the meniscus at the upper and lower calibration marks must be used to obtain the most precise results.

NOTE 4 - Use of more dilute sodium thiosulfate, e.g., 0.005N, increases the precision of the titration. This solution is prepared by diluting 50 ml sodium thiosulfate stock solution to a liter with reagent water.

#### 10. Calculations

If 0.025N sodium thiosulfate is used to titrate 200 ml of the original sample, each ml is equivalent to 1 mg/1 DO. If 0.005N sodium thiosulfate is used, each ml is equivalent to 0.2 mg/1 DO.

#### 11. Precision and Accuracy

Precision and accuracy vary with interferences and technique.

### SECTION 16. FLUORIDE IN SEA WATER

#### 1. Scope and Application

This method outlines the determination of fluoride in sea water. The method is applicable to sea water and product water.

#### 2. Principle of Method

Fluoride in an acidic sample is isolated by distillation as hydrofluorosilicic acid and determined colorimetrically as the zirconium-alizarin complex.

#### 3. Interferences

Interferences present in sea water are color, turbidity, sulfates, and chlorides. Color and turbidity are removed by distillation. Sulfate interference is eliminated by careful selection of the distillation apparatus and controlling the temperature range of the distillation. The critical points in the design of the apparatus are the diameter and slope of the delivery tube, the distance between the surface of the sample when boiling and the lower end of the delivery tube

and the fit of ground-glass joints. Interference from chlorides is avoided by the addition of silver sulfate to the sample.

#### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

#### 5. Apparatus

a. Fluoride Distillation Apparatus - similar to Scientific Glass Apparatus Company's Catalog #JD2130.

b. Nessler Color Comparison Tubes - matched tubes of 100 ml capacity with visual comparator.

#### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

#### 7. Reagents

a. Phenolphthalein Indicator Solution: Dissolve 0.5 g phenolphthalein in 50 ml of 95% ethyl alcohol and dilute to 100 ml with reagent water.

b. Silver Sulfate ( $\text{Ag}_2\text{SO}_4$ ), powder.

c. Sodium Hydroxide ( $\text{NaOH}$ ), pellets.

d. Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ), conc.

e. Sodium Arsenite Solution: Dissolve 2 g of sodium arsenite ( $\text{NaAsO}_2$ ) in reagent water and dilute to 1 liter.

f. Sodium Fluoride Standard Solution: Dissolve 0.221 g of sodium fluoride ( $\text{NaF}$ ) in reagent water and dilute to 1 liter. Dilute 100 ml of this solution to 1 liter with reagent water and store in a polyethylene bottle. 1 ml of this solution contains 0.01 mg F.

g. Sodium Hydroxide Solution: Dissolve 20 g of sodium hydroxide ( $\text{NaOH}$ ) in reagent water and dilute to 1 liter.

h. Sulfuric Acid (1:17): Slowly add, with mixing, 1 volume of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to 17 volumes of reagent water.

i. Zirconium-Alizarin Reagent: Dissolve 1.84 g of zirconyl nitrate ( $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ) or 2.22 g of zirconyl chloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) in 250 ml of reagent water. (See Note 1.) Dissolve 0.37 g of alizarin monosodium sulfonate in 250 ml of reagent water. Add 25 ml of the zirconyl solution to 50 to 100 ml of reagent water. Then, slowly, with constant stirring, add 25 ml of the alizarin solution and dilute to 500 ml with reagent water. Mix well and add 500 ml of 1:17  $\text{H}_2\text{SO}_4$ . (See Note 2.)

NOTE 1 - If the zirconyl solution is turbid, it should not be filtered. Turbidity at this point may be due to insolubility of the zirconyl salt. However, if the turbidity persists after mixing with the alizarin and acid solution, the reagent should be discarded. Impure chemicals will cause turbidity in the final reagent.

NOTE 2 - The acid indicator is ready for use after 1 hour. When stored in a dark bottle, the reagent is quite stable. A new reagent should be prepared if a precipitate forms or the color range becomes poor.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Procedure

### a. Steam Distillation - (See Note 3 and Figure 4.)

Add a 200 ml sample to the fluoride distillation flask and make alkaline to phenolphthalein with a pellet of NaOH. Add glass beads and concentrate to 15 to 20 ml using a hot plate with asbestos pad or a heating mantel. Allow the concentrated sample to cool. Then make the sample slightly acidic by dropwise addition of conc.  $\text{H}_2\text{SO}_4$ . Add sufficient  $\text{Ag}_2\text{SO}_4$  to precipitate the chloride present. (For sea water, approximately 23 grams are required. A slight excess is not harmful.) Connect the fluoride distillation flask to the condenser and a 200 ml receiving flask. Start a flow of cooling water through the condenser. Using a separatory funnel, slowly add 20 ml of conc.  $\text{H}_2\text{SO}_4$  through the steam inlet to the fluoride distillation flask. Remove the separatory funnel and insert the steam inlet tube. Connect the inlet to the steam generating flask. (A steam trap can be used between the steam generating flask and the fluoride distillation flask.) Make the water in the steam generator slightly alkaline to phenolphthalein with a NaOH pellet. Open the bypass and heat with a burner, hot plate, or heating mantel until steam is produced. Heat the contents of the fluoride distillation flask to  $135^\circ\text{C}$  with a hot plate or heating mantel. When this temperature is reached, open the steam inlet to the flask and close the steam bypass. Maintain a temperature of  $135^\circ\text{C}$  -  $145^\circ\text{C}$  and a distillation rate of at least 3 ml per minute by adjusting the steam flow (see Note 4) and applying heat to the fluoride distillation flask. Collect 200 ml of distillate.

NOTE 3 - Prior to each analysis, the apparatus should be cleaned. The fluoride distillation assembly should be washed with hot NaOH solution (10 percent) and rinsed with reagent water. Then heat conc.  $\text{H}_2\text{SO}_4$  to fumes in the flask, cool, and rinse thoroughly with reagent water.

NOTE 4 - A thistle tube may be used in the steam generating flask to aid in regulating the steam flow. Generally, with proper adjustment of the fluoride distillation flask heater, a water pressure of 6 to 8 inches in the thistle tube should be maintained.

#### b. Visual Comparison

Transfer 100 ml of the distillate or an aliquot containing less than 0.14 mg F to a Nessler tube. Dilute to 100 ml with reagent water if necessary. Remove any chlorine that is present by adding 0.1 ml  $\text{NaAsO}_2$  solution for each 0.1 mg of chlorine in the sample plus 0.1 ml excess.

Prepare a series of standards ranging from 0.1 mg F to 0.2 mg F in 100 ml reagent water using the NaF standard solution. The sensitivity of the visual comparison is dependent upon the increments used in preparing the standards. For sea water increments of 0.01 mg F are recommended.

Add exactly 10 ml of the zirconium-alizarin reagent to the sample and standards. Mix well and compare after 1 hour reaction time. A more satisfactory procedure is to allow a 7 to 18 hour reaction time if the results are not needed sooner. When the reaction time exceeds 7 hours, differences up to 1 hour in the ages of samples and standards are permissible. This allows the analyst to inspect the sample and repeat the color development on a smaller aliquot if the fluoride concentration of the original aliquot is too high.

After a suitable reaction time, compare the sample and standards using a comparator.

#### 10. Calculations

No calculations are necessary. The ppm fluoride is determined by matching the color developed in the sample with that of a standard.

#### 11. Precision and Accuracy

Precision and accuracy depend upon selection of apparatus and increments used in preparing standards. Using the procedure outlined, results can be reproduced within 0.05 ppm when analyzing sea water.

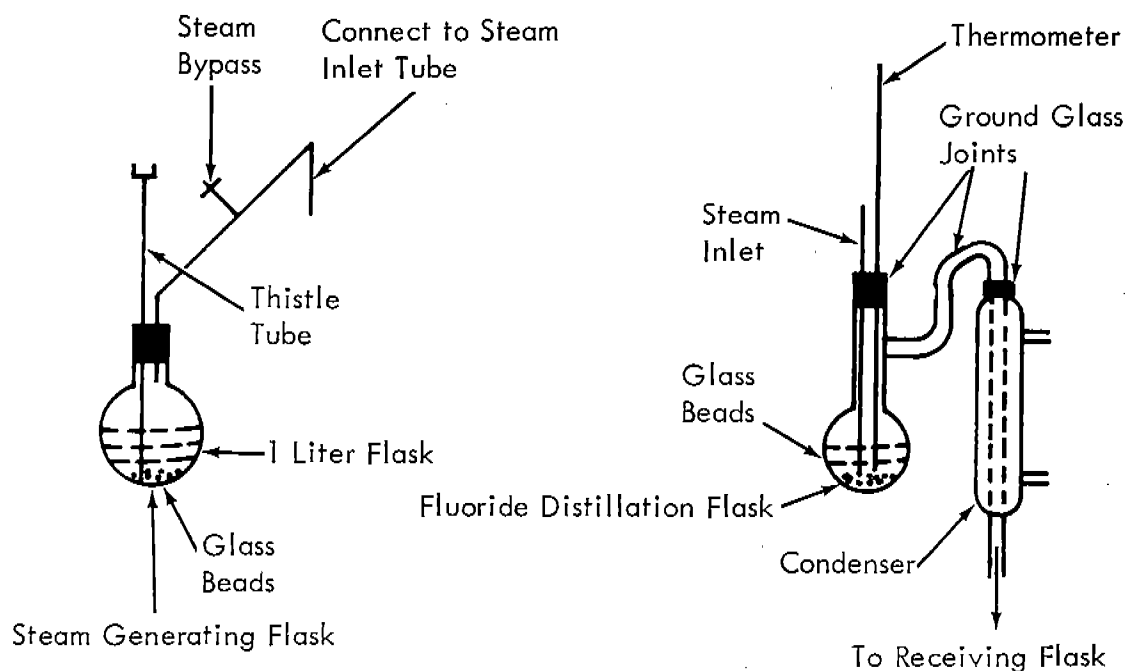


Figure 4. Sketch of Fluoride Distillation Assembly

## SECTION 17. IRON IN SEA WATER

### 1. Scope and Application

This method outlines the determination of total and dissolved iron in sea water. The method is applicable to sea water and product water where iron concentrations are in the 0.02 to 4.0 mg/l range. Where iron concentrations are lower such as in sea water not in contact with sources of iron, extraction of the phenanthroline complex may be necessary to increase sensitivity. Such a method is outlined in ASTM Designation: D1497-57T, "Iron in High Purity Industrial Waters."

## 2. Principle of Method

Solution of iron and reduction to the ferrous state is accomplished by boiling with acid and hydroxylamine hydrochloride. Treatment with 1,10-phenanthroline yields an orange-red complex which is formed when three (3) molecules of phenanthroline chelate an atom of ferrous iron. The complex in solution obeys Beer's Law, and its intensity is independent of pH 3 to 9 and is stable for 6 months. In the presence of excess phenanthroline, rapid color development can be obtained between pH 2.9 and 3.5. Detectable concentrations are 0.02 to 4.0 mg/l. Higher concentrations can be determined by using aliquots.

## 3. Interferences

Sea water, when using this method, is normally free of interferences. Color and organic matter which may be present at times may be removed by evaporation, ashing, and redissolving in acid.

## 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

## 5. Apparatus

- a. Spectrophotometer for use at 510 mμ.
- b. 1, 2, 10, and 50 ml pipets.
- c. 50 ml volumetric flasks.
- d. 125 ml erlenmeyer flasks.

## 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water." In addition, for this analysis, reagent water shall mean distilled water that has been deionized to give iron-free water.

## 7. Reagents

Hydroxylamine hydrochloride and phenanthroline solutions are stable for several months. Working iron solutions should be prepared from stock solution as needed. Other solutions are stable indefinitely.

a. Hydrochloric Acid, conc.

b. Hydroxylamine Hydrochloride: Dissolve 10 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  in 100 ml of reagent water.

c. Ammonium Acetate Buffer Solution: Dissolve 250 g  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  in 150 ml reagent water. Add 700 ml glacial acetic acid and dilute to 1 liter with reagent water.

d. Phenanthroline Solution: Dissolve 0.1 g 1, 10-phenanthroline monohydrate,  $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$ , in 100 ml reagent water with 2 drops conc. HCl added. Solution must be clear. One (1) ml of the reagent is sufficient for no more than 0.1 mg Fe.

e. Iron Stock Solution: Clean electrolytic iron wire with sandpaper to produce a bright surface. Weigh 0.2000 g and dissolve in 6N  $\text{H}_2\text{SO}_4$ . Dilute to 1 liter with reagent water. This solution contains 0.20 mg Fe per ml. Ferrous ammonium sulfate can be used to prepare the stock solution by dissolving 0.7022 g in 20 ml conc.  $\text{H}_2\text{SO}_4$  and 50 ml reagent water. Add 0.1N  $\text{KMnO}_4$  until a faint pink persists and dilute to 1 liter. This solution contains 0.10 mg Fe per ml.

f. Iron Working Solution: Prepare daily from stock solution as needed. Dilute 50 ml of iron wire stock solution or 100 ml ferrous ammonium sulfate stock solution to 1 liter with reagent water. This solution contains 0.010 mg Fe per ml. Dilute 5 ml of iron wire stock solution or 10 ml ferrous ammonium sulfate stock solution to 1 liter. This solution contains 0.001 mg Fe per ml.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis. Immediately acidify samples to pH 3.3 to 3.7 with HCl to prevent precipitation or plating of iron.

## 9. Calibration and Standardization

Prepare a series of standards, ranging from 0.001 to 0.10 mg Fe, by accurately pipeting calculated volumes of working solutions into 125 ml erlenmeyer flasks using the weaker working solution (0.001 mg per ml) to prepare the 0.001 - 0.010 mg standards. Dilute to 50 ml and treat as described in the procedure for total iron. The standards are read against reagent water set at zero absorbance and a calibration curve plotted, including a blank (reagent water treated to correct for iron in the reagent water and reagents). If color or turbidity interfere, samples can be taken through all the steps of the procedure except addition of phenanthroline. Each developed sample, with phenanthroline, is read against the corresponding blank without phenanthroline.

## 10. Procedure

a. Total iron: Mix the sample thoroughly and pipet 50 ml or an aliquot containing not more than 0.1 mg Fe into a 125 ml erlenmeyer flask. Dilute to 50 ml if necessary and add 2-5 drops conc. HCl and 1 ml hydroxylamine hydrochloride solution. (NOTE: 2 ml conc. HCl can be added if necessary to dissolve the iron. If this is done when analyzing sea water, a pH adjustment will be required before addition of phenanthroline to obtain the pH range 2.9 - 3.5 for color development.) Add glass beads and reduce volume to 15-20 ml by boiling. Cool to room temperature and transfer to a 50 ml volumetric flask. Add 10 ml acetate buffer solution and 2 ml phenanthroline solution. Dilute to the mark with reagent water, mix thoroughly, and allow 10 minutes for maximum color development.

b. Dissolved iron: Allow the sample to settle and decant through a fine filter paper (Whatman #42). Treat a measured volume as described in the procedure for total iron.

## 11. Calculations

ppm Fe is determined by comparison of observed readings with the calibration curve and using the following equation:

$$\text{mg/l (ppm) Fe} = \frac{\text{mg Fe (from curve)} \times 1,000}{\text{ml sample}}$$

## 12. Precision and Accuracy

Using a spectrophotometer, the reliability of this method is approximately 1 percent or 0.001 mg whichever is the greater. Results can be reproduced to within 0.02 ppm.

# SECTION 18. LEAD IN SEA WATER

## 1. Scope and Application

This method outlines the procedure for determining lead in sea water. The method is applicable to sea water and product water.

## 2. Principle of Method

Lead in basic solution will form a red chelated complex with dithizone. The complex is soluble in chloroform or carbon tetrachloride but insoluble in water. The color change in organic solvent is green to red depending on the lead concentration.

### 3. Interferences

Copper, zinc, iron, bismuth, thallium, and stannous tin will interfere with the color development. Hydroxylamine hydrochloride is added to inhibit the oxidation of dithizone by ferricyanide formed by iron. In sea water, copper, zinc, bismuth, thallium, and stannous tin are not normally present in sufficient quantity to interfere.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

- a. Separatory Funnels (100-125 ml) and miscellaneous glassware.
- b. Spectrophotometer for use at 510 m $\mu$ .

### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

### 7. Reagents

a. Nitric Acid (HNO<sub>3</sub>), 1%: Add 10 ml conc. HNO<sub>3</sub> to approximately 200 ml reagent grade water and dilute to 1 liter with reagent grade water.

b. Ammonium Hydroxide (NH<sub>4</sub>OH), conc.

c. Hydroxylamine Hydrochloride (NH<sub>2</sub>OH·HCl), 20%: Dissolve 20 g NH<sub>2</sub>OH·HCl in 50-75 ml reagent grade water. Make the solution alkaline to thymol blue with conc. NH<sub>4</sub>OH. Add 5 ml of 4% sodium diethyldithiocarbamate. Allow to stand 5-10 minutes. Extract with 25 ml of CCl<sub>4</sub>. Repeat the extraction with CCl<sub>4</sub> until no color is evident in the CCl<sub>4</sub> layer when the layer is shaken with a dilute solution of a copper salt. Make the NH<sub>2</sub>OH·HCl solution just acid with HCl and dilute to 100 ml with reagent grade water.

d. Thymol Blue Indicator Solution: Dissolve 0.1 g thymol blue in 21.5 ml 0.01N NaOH and dilute to 250 ml with reagent grade water.

e. Ammonium Citrate, (NH<sub>4</sub>)<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, 50%: Dissolve 50 g (NH<sub>4</sub>)<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> in 100 ml reagent grade water. Adjust the pH to 8.5 - 9.0 with NH<sub>4</sub>OH. Extract with successive portions of dithizone, 0.005%, until all lead has been removed

as evidenced by a green color in the dithizone extract. Remove excess dithizone by extracting with  $\text{CCl}_4$ .

f. Dithizone, 0.005%: Dissolve 50 mg of diphenylthiocarbazone in 1 liter  $\text{CCl}_4$ . Keep tightly stoppered and store in a refrigerator.

g. Potassium Cyanide (KCN), 10% (See Note 1): Dissolve 50 g KCN in 500 ml reagent grade water. Remove any lead by repeated extractions with dithizone. The excess dithizone is removed by extraction with  $\text{CHCl}_3$ .

h. Ammoniacal - Cyanide Solution: Dissolve 10 g KCN in 500 ml conc.  $\text{NH}_4\text{OH}$ . Add 10 g citric acid and dilute to 1 liter with reagent grade water.

i. Standard Lead Solutions: Dry approximately 1 g lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) at  $110^\circ\text{C}$  for 2 hours. From this, weigh exactly 0.1599 g and dissolve in 500 ml of 1:99  $\text{HNO}_3$ . 1 ml of this solution is equivalent to 0.200 mg Pb. Dilute 50 ml of this standard to 1 liter with reagent grade water. 1 ml of this solution is equivalent to 0.010 mg Pb.

NOTE 1 - CAUTION: Cyanide compounds are extremely poisonous. All work areas must be kept clean of spills. Do not pour cyanide solutions down acid drains. Always use a hood when preparing or working with cyanide solution due to the possible evolution of cyanide gas.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Calibration and Standardization

Prepare a series of standards over the range of 0-1 ppm Pb using the standard lead solutions. Treat 50 ml of the standards and a reagent grade water blank as described under Procedure. Measure the absorbance of the standards against the blank. Plot the measured absorbance vs. mg Pb.

## 10. Procedure

This procedure is extremely sensitive. All glassware must be thoroughly cleaned then soaked and rinsed in dilute nitric acid prior to use.

Pipet 50 ml of the sample, or an aliquot containing less than 0.02 mg Pb, into a separatory funnel. Dilute to 50 ml with reagent grade water if necessary. Treat the sample and 50 ml reagent grade water as described below.

Add 10 ml ammonium citrate solution and 2 ml hydroxylamine hydrochloride solution. Add 10 drops thymol blue indicator solution and make alkaline with conc.  $\text{NH}_4\text{OH}$ .

CAUTION: In the following steps of the procedure, use a hood. Add 4 ml 10% KCN. Adjust the pH to 8.5 - 9.0 with 1% HNO<sub>3</sub>. Extract with 5 ml portions of the dithizone solution. Drain each extract into another separatory funnel. Continue the extractions until all Pb has been removed as evidenced by the dithizone solution retaining its original green color. Remove the Pb from the combined dithizone extracts by shaking with 20 ml 1% HNO<sub>3</sub>. Discard the CCl<sub>4</sub> layer. Dilute to 50 ml with 1% HNO<sub>3</sub>. Add 4 ml of the ammoniacal-cyanide solution and 5 ml dithizone solution. Immediately shake for 1 minute. Measure the absorbance of the sample against the blank using a spectrophotometer at 510 mμ.

#### 11. Calculations

ppm Pb is determined by comparison of observed absorbance with the calibration curve and using the following equation:

$$\text{mg/l Pb} = \frac{\text{mg Pb (from curve)} \times 1,000}{\text{ml sample}}$$

#### 12. Precision and Accuracy

Results are accurate and reproducible to  $\pm 0.002$  mg Pb.

### SECTION 19. MANGANESE IN SEA WATER

#### 1. Scope and Application

This method outlines the procedure for determining manganese in sea water. The method is applicable to sea water and product water.

#### 2. Principle of Method

Manganese is determined colorimetrically by persulfate oxidation of soluble manganous compounds to form permanganate. The oxidation is carried out in the presence of silver nitrate. When excess persulfate is present and organics are absent, the resulting color is stable for 24 hours. The minimum detectable concentration of Mn is 0.005 mg.

#### 3. Interferences

Interferences include chlorides, bromides, and iodides. Mercuric sulfate is added to minimize these interferences; however, due to the high chloride concentration in sea water, the effect of this interference is not completely

eliminated. When using this method, the analyst must add known amounts of Mn to sea water samples and measure the difference in absorbance compared to sea water samples to which Mn has not been added. Organic matter will also interfere but can be eliminated by increasing the heating period and the amount of persulfate which is added. Hydrogen peroxide is added when measuring absorbance to correct for "apparent" Mn.

#### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

#### 5. Apparatus

- a. Spectrophotometer for use at 525 mμ.
- b. Miscellaneous glassware.
- c. Heater-stirrer combination.

#### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

#### 7. Reagents

- a. Ammonium Persulfate.
- b. Hydrogen Peroxide Solution, 30%.
- c. Special Solution: Dissolve 75 g mercuric sulfate in 400 ml conc.  $\text{HNO}_3$  and 200 ml reagent water. Add 200 ml 85%  $\text{H}_3\text{PO}_4$  and 0.35 g silver nitrate. Cool and dilute to 1 liter with reagent water.
- d. Standard Manganese Solution: Dissolve 3.2 g  $\text{KMnO}_4$  in 1 liter reagent water. Heat 4-6 hours near the boiling point, then filter through a fritted-glass filter. Standardize against sodium oxalate using the following procedure: Weigh several samples of previously dried sodium oxalate into 400 ml beakers. The samples should weigh 0.1 - 0.2 g and be weighed to the nearest 0.1 mg. To each sample add 100 ml reagent water and stir to dissolve. Add 10 ml 1:1  $\text{H}_2\text{SO}_4$  and heat rapidly to 90-95°C. Standardize the permanganate solution by titrating the oxalate samples rapidly while stirring. A stirrer - hot plate combination should be used since the temperature must not fall below 85°C during the titration. The end point is a slight, pink color that persists for at least 1

minute. Calculate the volume of permanganate required to prepare 1 liter the strength of which is 1 ml = 0.05 mg Mn using the following equation:

$$\text{ml KMnO}_4 = \frac{4.55}{\text{normality KMnO}_4}$$

To the calculated volume add 2-3 ml conc.  $\text{H}_2\text{SO}_4$  and 100 ml sodium bisulfite solution (10 g  $\text{NaHSO}_3$  dissolved in 100 ml reagent water). Add the bisulfite solution dropwise, stirring until the permanganate color disappears. Remove excess  $\text{SO}_2$  by boiling and then cool and dilute to 1 liter with reagent water.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Calibration and Standardization

Prepare a series of standards containing 0.005 - 1.5 mg Mn. Treat these and a reagent water blank as outlined in Procedure and plot measured absorbance against mg Mn.

## 10. Procedure

To a 100 ml sample, add 5 ml of the "special solution." Concentrate the sample to 90 ml by boiling. Add 1 g ammonium persulfate and quickly (within 2 minutes) bring to a boil over a flame. Immediately upon boiling, remove the sample and let stand for 1 minute. Cool under a faucet, dilute to 100 ml with reagent water and mix. Measure the absorbance against a blank of reagent water which has been treated in the same manner. Use a spectrophotometer with a wavelength setting of 525 m $\mu$ . After the initial absorbance reading has been taken, add 1 drop hydrogen peroxide solution to the sample absorption cell. Mix and when the permanganate color has completely faded, measure the absorbance again. The difference between the initial and second absorbance readings is "apparent" manganese or "interferences as manganese."

## 11. Calculations

mg/l Mn is determined by comparison of observed absorbance with the calibration curve and using the following equation:

$$\text{mg/l Mn} = \frac{\text{mg Mn (from curve)} \times 1,000}{\text{ml sample}}$$

## 12. Precision and Accuracy

Results are reproducible to  $\pm 0.01$  mg Mn.

## SECTION 20. NICKEL IN SEA WATER

### 1. Scope and Application

This method outlines the procedure for determining nickel in sea water. The method is applicable to sea water and product water.

### 2. Principle of Method

Nickel forms a complex with ammoniacal dimethylglyoxime in the presence of iodine. The color is measured with a spectrophotometer at 530 mμ.

### 3. Interferences

The addition of ammonium citrate eliminates iron interference. Copper will interfere if present in amounts greater than 3 ppm.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

- a. Spectrophotometer for use at 530 mμ.
- b. Separatory funnels, 125 ml, ground glass stopper.
- c. Miscellaneous glassware.

### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water." In addition, for this analysis, reagent water shall mean distilled water that has been redistilled using glass apparatus or deionized to give iron and copper-free water.

### 7. Reagents

a. Ammonium Citrate Solution: Dissolve 500 g of citric acid monohydrate in 675 ml of conc.  $\text{NH}_4\text{OH}$ . Cool and dilute to 1000 ml with reagent water. Filter, if necessary, to remove suspended particles.

b. Ammonium Hydroxide, 1:1: Mix equal volumes of conc.  $\text{NH}_4\text{OH}$  and reagent water and filter.

c. Dimethylglyoxime, Ammoniacal Solution: Dissolve 1 g of dimethylglyoxime in 500 ml conc.  $\text{NH}_4\text{OH}$ . Add 500 ml reagent water and filter. Prepare fresh after two weeks.

d. Iodine Solution: Dissolve 6.35 g of iodine in a solution of 75 g KI in 60 ml reagent water and dilute to 500 ml with reagent water. Store in a dark, stoppered bottle.

e. Nickel Standard, 1 ml = 0.02 mg Ni: Place 1 g of Ni (not less than 99.9 percent Ni) in a 250 ml beaker and add 10 ml reagent water and 10 ml conc.  $\text{HNO}_3$ . Cover with a watch glass and allow to stand until dissolved. Add 1 ml conc.  $\text{H}_2\text{SO}_4$  and evaporate to just short of complete dryness. Cool, add 5 ml conc.  $\text{H}_2\text{SO}_4$ , and evaporate to dense, white fumes. (Caution: Boil slowly to prevent losses.) Using a volumetric flask, dilute to 500 ml with reagent water. Dilute 50 ml to 1 liter with reagent water in a volumetric flask and finally dilute 50 ml of this solution to 250 ml in a volumetric flask.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Sample shall be at room temperature prior to beginning the analysis.

## 9. Calibration and Standardization

Prepare a series of standards ranging from 0.02 to 0.25 mg Ni by pipeting aliquots of the standard nickel solution into 100 ml volumetric flasks. Dilute with reagent water to approximately 50 ml and continue as outlined under Procedure. Plot absorbance against mg Ni on linear paper, using the vertical scale for absorbance.

## 10. Procedure

Measure 50 ml portions of the sample into each of two 100 ml volumetric flasks. Add 10 ml of the ammonium citrate solution and 5 ml of the iodine solution to each flask. To one flask add 20 ml of ammoniacal dimethylglyoxime solution and dilute to 100 ml with reagent water. Allow to stand 10 minutes. To the other flask add 20 ml 1:1  $\text{NH}_4\text{OH}$ . Dilute to 100 ml with reagent water and allow to stand 10 minutes. Use this solution as the reference. Using a spectrophotometer set at 530 m $\mu$ , measure the absorbance of the sample versus the reference. Absorbances of standards and additional samples are measured similarly.

## 11. Calculations

$$\text{mg/l (ppm) Ni} = \frac{\text{mg Ni (from curve)} \times 1,000}{\text{ml sample}}$$

## 12. Precision and Accuracy

Results can be reproduced to within 0.01 mg.

# SECTION 21. OIL AND GREASE IN SEA WATER

## 1. Scope and Application

This method outlines the determination of oils in sea water. The method is applicable to sea water, product water, and effluent water.

## 2. Principle of Method

Dissolved or emulsified oil or grease is extracted from water with an organic solvent. The solvent is evaporated and the residue is weighed.

## 3. Interferences

This method is not selective for oil and grease. Other organic substances may be extracted depending upon the solvent used.

## 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

## 5. Apparatus

- a. Separatory Funnel - 1 liter, Teflon stopcock.
- b. Graduated Cylinders - 50 and 500 ml.
- c. Pipet - 5 ml graduated.
- d. Beakers - 150 and 200 ml.
- e. Fritted Glass Funnel - coarse, 60 ml.

## 6. Purity of Reagents

Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

## 7. Reagents

- a. Ethyl Ether or Chloroform
- b. Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ), conc.
- c. Sodium Sulfate ( $\text{Na}_2\text{SO}_4$ ), anhydrous granular

## 8. Sampling

Samples shall be taken in clean glass bottles. In addition to normal cleaning, sample bottles shall be rinsed with solvent and air dried. Do not completely fill sample bottle since loss of floating oil may occur when stoppering. Care shall be taken to insure that the sample is representative.

## 9. Procedure

Using a 500 ml graduated cylinder, add 500 ml of the sample to a 1 liter separatory funnel. Acidify with 2.5 ml conc.  $\text{H}_2\text{SO}_4$ . Rinse the graduate with 10 ml solvent (see Note 1) and add to the separatory funnel.

Extract with 50 ml solvent, shaking vigorously for 2 minutes. CAUTION: Vent by opening stopcock several times during shaking to expel gases. Allow the layers to separate then withdraw the aqueous layer into a clean beaker. Transfer the solvent layer to a 200 ml beaker and repeat the extraction of the aqueous layer twice using 25 ml solvent each time.

Combine the solvent layers and filter through a fritted glass funnel containing anhydrous  $\text{Na}_2\text{SO}_4$ . Catch the filtrate in a previously dried and weighed 150 ml beaker. Rinse the 200 ml beaker with 10 ml solvent. Filter and collect in the tared 150 ml beaker.

Evaporate the solvent by air drying in a fume hood then place the beaker in a desiccator. After 1 hour, weigh the beaker and contents.

NOTE 1 - Use either ethyl ether or chloroform as solvent. Observe safety precautions when using solvents particularly ethyl ether.

## 10. Calculations

$$\text{Oils and grease, mg/l} = \frac{(A - B) \times 1,000}{\text{ml sample}}$$

Where,

A = Weight of tared beaker and residue after evaporation

B = Initial weight of tared beaker

## 11. Precision and Accuracy

For small quantities of oil and grease, the technique of the analyst will govern the accuracy of the analysis.

## SECTION 22. PHOSPHATES IN SEA WATER

### 1. Scope and Application

This method outlines the procedure for determining total phosphates in sea water. The method is applicable to sea water and product water.

### 2. Principle of Method

The meta-, pyro-, and polyphosphates are determined. Soluble orthophosphates and organic phosphorous compounds which are oxidizable to orthophosphate are also determined. The procedure includes acid digestion to decompose organic compounds and oxidation of the various phosphates to orthophosphate. The orthophosphate is then converted to phosphomolybdate by acidified ammonium molybdate reagent. A blue color is developed when the phosphomolybdate is reduced with stannous chloride. The minimum detectable concentration is 0.01 mg/l  $\text{PO}_4$ .

### 3. Interferences

Interferences which are present in sea water include iron, turbidity, and color. Color, turbidity, and insoluble iron can be eliminated by filtration. Silica gives a pale, blue color which is additive to the phosphate color. If maximum accuracy is desired, a separate sample should be analyzed for silica and the phosphate concentration adjusted.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

- a. Steam Bath
- b. Miscellaneous Glassware
- c. Spectrophotometer for use at 700 m $\mu$ .

## 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

## 7. Reagents

a. Sulfuric Acid, 3.6N: Add 10 ml conc.  $\text{H}_2\text{SO}_4$  to reagent water and dilute to 100 ml.

b. Sulfuric Acid, 0.05N: Dilute 1.4 ml 3.6N  $\text{H}_2\text{SO}_4$  to 100 ml.

c. Sulfuric Acid, 20N: Add 112 ml conc.  $\text{H}_2\text{SO}_4$  to reagent water and dilute to 200 ml.

d. Sodium Hydroxide, 1N: Dissolve 40 g NaOH pellets in 1 liter reagent water.

e. Phenolphthalein Indicator Solution: Dissolve 2.5 g phenolphthalein in 500 ml 50% ethyl alcohol (or denatured). Neutralize with 0.02N NaOH.

f. Ammonium Molybdate Solution, 5%: Dissolve 10 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in reagent water and dilute to 200 ml.

g. Molybdate Reagent: Mix equal volumes of 5% ammonium molybdate and 20N  $\text{H}_2\text{SO}_4$ . Due to the instability of this reagent, it should be prepared immediately before use.

h. Stannous Chloride Solution, 0.25%: Dissolve 2.5 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and 10 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  in 20 ml conc. HCl which has been diluted to 1 liter with reagent water.

i. Standard Phosphate Solution: Dissolve 0.1433 g of previously dried  $\text{KH}_2\text{PO}_4$  in reagent water. Add 2-3 drops chloroform and dilute to 1 liter. 1 ml of this solution contains 0.1 mg  $\text{PO}_4$ .

j. Standard Phosphate Solution: Dilute 50 ml of the 1 ml = 0.1 mg  $\text{PO}_4$  standard to 1 liter with reagent water. 1 ml of this solution contains 0.005 mg  $\text{PO}_4$ .

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Calibration and Standardization

Prepare a series of standards covering the desired  $\text{PO}_4$  concentration range. In sea water, 0.01 to 1 mg/l  $\text{PO}_4$  is usually adequate. Adjust the volumes to 25 ml with reagent water. To the standards and a blank of 25 ml reagent water add 1 ml molybdate reagent and mix. After 5 minutes and before 10 minutes, add 1 ml 0.25%  $\text{SnCl}_2$ . Measure the absorbance of the standards against the blank after 30-45 minutes. (See Note 3.) Use a spectrophotometer with wavelength setting of 700 m $\mu$ . Plot the absorbance vs. mg  $\text{PO}_4$ .

## 10. Procedure (See Note 1)

Pipet 100 ml of the sample, which has been filtered if necessary to remove color and turbidity, into a 250 ml erlenmeyer flask. Add 3 ml conc. HCl and 0.5 ml conc.  $\text{HNO}_3$ . Digest on a steam bath 2-3 hours. Remove the sample from the steam bath and evaporate to approximately 50 ml over a small flame. Add 4 ml 3.6N  $\text{H}_2\text{SO}_4$  and evaporate to approximately 3 ml. (See Note 2.) Cool and dilute to 20 ml with reagent water. Add 1-3 drops phenolphthalein indicator and titrate with 1N NaOH to a pale, pink color. Add 0.05N  $\text{H}_2\text{SO}_4$  dropwise until the pink color just disappears. Adjust the volume to 25 ml. To the sample and a blank (25 ml reagent water) add 1 ml molybdate reagent and mix. After 5 minutes and before 10 minutes, add 1 ml 0.25%  $\text{SnCl}_2$ . Measure the absorbance of the sample against the blank after 30-45 minutes. (See Note 3.) Use a spectrophotometer with wavelength setting of 700 m $\mu$ .

NOTE 1 - This method is extremely sensitive. All glassware must be thoroughly cleaned and rinsed before using.

NOTE 2 - The acid will fume at this point. Do not let portions of the bottom of the flask become dry.

NOTE 3 - The time delay selected for measuring absorbance of the sample should approximate that used when preparing the calibration curve.

## 11. Calculations

$$\text{mg/l PO}_4 = \frac{\text{mg PO}_4 \text{ (from curve)} \times 1,000}{\text{ml sample}}$$

## 12. Precision and Accuracy

Precision and accuracy depend largely on technique, apparatus, and cleanliness of glassware.

## SECTION 23. SILICA IN SEA WATER

### 1. Scope and Application

This method outlines procedures for determining total and soluble silica in sea water. The method is applicable to sea water and product water.

### 2. Principle of Method

#### a. Total Silica

Total silica is determined gravimetrically by concentration and precipitation. Dissolved or suspended silica compounds are precipitated as partially dehydrated silica by evaporation with perchloric acid. The residue is ignited to constant weight, and the silica volatilized to silicon tetrafluoride. Silica in concentrations as low as 1 ppm can be determined accurately.

#### b. Soluble Silica

Soluble silica is determined colorimetrically by reaction with molybdate ion in acidic solution. The molybdate ion forms a greenish-yellow complex with silica. The reaction does not follow Beer's Law perfectly. The sensitivity of the method may be increased when measuring silica concentrations less than 2 ppm by adding amino-naphthol-sulfonic acid. A blue color is produced.

### 3. Interferences

#### a. Total Silica

Generally, no interferences are present in sea water.

#### b. Soluble Silica

Color and turbidity interfere but are not normally present in sufficient quantity to affect sea water analysis.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

#### a. Spectrophotometer

#### b. Infrared lamps

#### c. Desiccator

#### d. Hot plate

- e. Teflon evaporating dishes (400 ml)
- f. Miscellaneous glassware, platinum crucibles, and filter paper
- g. Fisher burners

## 6. Purity of Reagents

a. - Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

In addition, silica-free water shall be prepared for use as reagent water by deionization of previously distilled water.

## 7. Reagents

### a. Total Silica

- (1) Hydrochloric Acid (HCl), conc.
- (2) Hydrochloric Acid (HCl), 1:49
- (3) Hydrofluoric Acid (HF), 48%
- (4) Nitric Acid (HNO<sub>3</sub>), conc.
- (5) Perchloric Acid (HClO<sub>4</sub>), 70%
- (6) Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>), conc.
- (7) Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>), anhydrous powder, reagent grade

### b. Soluble Silica

(1) Amino-naphthol-sulfonic Acid Solution: Dissolve 1 g of sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) and 0.5 g of 1-amino-2-naphthol-4-sulfonic acid in 50 ml reagent water. Add to this solution 100 ml of sodium hydrogen sulfite solution (30 g NaHSO<sub>3</sub> per 100 ml reagent water). Dilute to 200 ml with reagent water and store in a dark plastic bottle. Prepare a fresh solution every two weeks.

(2) Ammonium Molybdate Solution: Dissolve 10 g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O in 100 ml reagent water. Store in a plastic bottle. Adjust the pH to 7-8 with silica-free ammonium or sodium hydroxide.

(3) Oxalic Acid Solution: Dissolve 10 g H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in 100 ml reagent water. Store in a plastic bottle.

- (4) Hydrochloric Acid (HCl), conc.

(5) Standard Silica Solution: Dissolve 4.732 g of sodium metasilicate ( $\text{NaSiO}_3 \cdot 9\text{H}_2\text{O}$ ) in reagent water and dilute to 1 liter. Store in a plastic bottle. This solution contains 1 mg  $\text{SiO}_2$  per ml.

## 8. Sampling

Samples shall be taken in clean plastic bottles. Sample bottles must be thoroughly cleaned and soaked, preferably overnight, in 10% HF. Samples shall be at room temperature prior to beginning the analysis.

## 9. Calibration and Standardization

Prepare a series of standards in the 0-2 ppm range and another in the 2-20 ppm. Treat the 2-20 ppm standards as outlined in Section b, Paragraphs 1 and 2 under Procedure. The 0-2 ppm standards are treated as outlined in Section c under Procedure. The standards are read against reagent water set at zero absorbance and a calibration curve plotted, including a reagent water blank.

## 10. Procedure

### a. Total Silica

Add 5 ml conc. HCl to 300 ml sea water in a 400 ml Teflon evaporating dish. Using an infrared lamp, evaporate 1 liter of sea water to 50 ml adding an additional 10 ml conc. HCl during the evaporation. (See Note 1.) Add 15 ml conc. HCl and 5 ml conc.  $\text{HNO}_3$  and continue evaporation to approximately 20 ml. Transfer the Teflon dish and sample to a hot plate under the hood. Add 10 ml conc.  $\text{HNO}_3$  and 5 ml  $\text{HClO}_4$  (CAUTION: See Note 2) to the sample. Continue evaporation on the hot plate until dense, white  $\text{HClO}_4$  fumes appear and the sample begins boiling. Continue boiling for 10 minutes.

Cool the concentrated sample, add 50 ml reagent water, and boil for 10 minutes. Filter through a #42 Whatman filter paper. Wash the filter paper and residue thoroughly with hot 1:49 HCl to remove  $\text{HClO}_4$ .

Dry and char the paper in an oven without burning it. Place the filter paper containing the residue in a weighed, platinum crucible. Then ignite the crucible and contents over a Fisher burner. The residue will be white when ignition is complete. Cool in a desiccator and weigh. Continue ignition and weighing until a constant weight is obtained.

To the weighed residue in the platinum crucible, add 5 drops conc.  $\text{H}_2\text{SO}_4$  and 5 ml HF. Evaporate to dryness on a hot plate under a fume hood. Ignite the crucible and residue and weigh. Repeat until a constant weight is obtained.

The quantity of reagent water required for dilutions in the procedure is treated as a blank and silica determined.

NOTE 1 - To prevent contamination, carry the evaporation out in a hood. The infrared lamp will provide extra shielding from the atmosphere.

NOTE 2 - Addition of  $\text{HClO}_4$  must be carried out under a hood, shield down.  $\text{HClO}_4$  reacts explosively with organic matter which may be present at times in sea water. The presence of  $\text{HNO}_3$  prevents spontaneous reaction and explosion during evaporation with  $\text{HClO}_4$ .

b. Soluble Silica (greater than 2 ppm)

To a 50 ml aliquot of the sample, add rapidly 0.5 ml conc.  $\text{HCl}$  and 2 ml ammonium molybdate solution. Mix and allow to stand for 5 minutes. Add 1.5 ml oxalic acid solution. Measure the absorbance using a spectrophotometer at 410  $\text{m}\mu$  against a reagent water blank.

c. Soluble Silica (less than 2 ppm)

Treat a 50 ml aliquot of the sample and a reagent water blank as outlined in Section b, above.

One minute after addition of the oxalic acid solution, add 2 ml of the amino-naphthol-sulfonic acid solution. Allow 5 minutes for color development. Measure the absorbance using a spectrophotometer at 815  $\text{m}\mu$  against the blank.

## 11. Calculations

No calculation is required to determine the ppm soluble silica. The calibration curve is prepared in ppm.

$$\text{Total SiO}_2, \text{ ppm} = \frac{(W_1 - W_2) - (W_3 - W_4)}{V}$$

Where,  $W_1$  = Weight of crucible + sample residue, in mg, after 1st ignition

$W_2$  = Weight of crucible and sample residue, in mg, after HF ignition

$W_3$  = Weight of crucible and blank residue, in mg, after 1st ignition

$W_4$  = Weight of crucible and blank residue, in mg, after HF ignition

$V$  = Liters of sample evaporated

## 12. Precision and Accuracy

Precision and accuracy for total silica are dependent upon the balance and technique. Generally, sample results are reproducible to  $\pm 0.2$  ppm. In the

colorimetric methods, results are reproducible to 0.005 ppm in low concentrations when using 100 mm sample cells for measuring absorbance.

## SECTION 24. SULFATES IN SEA WATER

### 1. Scope and Application

This method outlines the procedure for determining the sulfate concentration in sea water. The method is applicable to the analysis of sea water and other waters where the sulfate concentration exceeds 10 mg/l.

### 2. Principle of Method

In an acid medium when barium chloride is added, sulfates are precipitated as barium sulfate. The precipitate is dried and weighed as barium sulfate. The sulfate concentration is calculated from this weight.

### 3. Interferences

Interferences include suspended matter, silica, sulfites, sulfides, and nitrates. These interferences lead to high results. Low results can be caused by iron, chromium, or other heavy metals. Suspended matter and silica interferences are removed in this method. Barium sulfate tends to occlude or adsorb other interferences; however, the precision and accuracy of the method is not significantly affected.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

- a. Drying oven for use at 80 - 90°C.
- b. Muffle furnace for use at 800°C.
- c. Desiccator.
- d. Gooch crucibles and suction apparatus.
- e. Analytical balance with sensitivity of 0.1 mg.
- f. Hot plate.
- g. Miscellaneous glassware.

- h. Ashless filter paper.
- i. Platinum crucibles.

## 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

## 7. Reagents

a. Hydrochloric Acid, 1:9: Add 1 volume conc. HCl to 9 volumes reagent water.

b. Methyl Orange Indicator: Dissolve 0.05 g of methyl orange in 100 ml of reagent water.

c. Barium Chloride Solution: Dissolve 100 g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in 1 liter of reagent water. Filter through a #40 Whatman filter paper. One (1) ml of this solution will precipitate approximately 40 mg  $\text{SO}_4$ .

d. Asbestos for Filter Mat: Add 15 g acid-washed medium filter asbestos to 1 liter of reagent water. Remove the fines by decantation.

e. Chloride Test Solution: Dissolve 8.5 g  $\text{AgNO}_3$  and 0.5 ml concentrated  $\text{HNO}_3$  in 500 ml reagent water.

f. Hydrofluoric Acid, concentrated.

g. Sulfuric Acid, concentrated.

h. Picric Acid, saturated aqueous solution.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Procedure

Interfering cations are removed by passing the sample through a cation removing ion-exchange column. Suspended matter is removed by filtering. Silica in excess of 25 mg per liter is removed as described in the procedure. A 50 ml aliquot of sea water is diluted to 250 ml and placed in a 400 ml beaker. Acidify the sample to the methyl orange end point with 1:9 HCl and then add 10 ml excess. Heat the solution to boiling and while stirring vigorously, slowly

add hot  $\text{BaCl}_2$  solution (see Note 1) until precipitation appears to be complete. Then add 2 ml excess.

NOTE 1 - Addition of 10 ml of the saturated picric acid solution and boiling before adding the  $\text{BaCl}_2$  solution will speed up precipitation and produce a coarser precipitate.

Allow the sample to digest at 80 - 90°C for at least 2 hours, preferably over night.

An asbestos filter mat in the Gooch crucible is prepared using suitable suction apparatus. Wash with hot reagent water, dry, and ignite at 800°C for 30 minutes. Cool the crucible in a desiccator and weigh.

Using the Gooch crucible, filter the  $\text{BaSO}_4$  suspension. Wash the precipitate with hot reagent water until the washings are substantially free of chlorides as indicated by the  $\text{AgNO}_3$  solution. (See Note 2.)

NOTE 2 - Complete elimination of chlorides by washing should not be attempted. Discontinue washing when the  $\text{AgNO}_3$  solution produces no more than a faint opalescence.

Dry the filter and precipitate and ignite at 800°C for 30 minutes. Cool in a desiccator and weigh.

If silica is present in concentrations exceeding 25 mg/l the  $\text{BaSO}_4$  suspension is filtered using an ashless filter paper instead of a Gooch crucible. The filter paper is charred in a weighed platinum crucible and ignited at 800°C for 1 hour. Add 1 drop concentrated  $\text{H}_2\text{SO}_4$  and 5-8 drops of HF to the residue and evaporate under a hood to expel silica as  $\text{SiF}_4$ . Reignite at 800°C for 30 minutes, cool in a desiccator, and weigh as  $\text{BaSO}_4$ .

#### 10. Calculations

The concentration of  $\text{SO}_4$  ion in ppm is calculated using the following equation:

$$\text{mg/l (ppm) SO}_4 = \frac{\text{mg BaSO}_4 \times 411.5}{\text{ml sample}}$$

#### 11. Precision and Accuracy

Precision and accuracy depend on the technique of the individual analyst. With proper technique, results can be reproduced to within 10 ppm when analyzing sea water.

## SECTION 25. SURFACTANTS (ANIONIC) IN SEA WATER

### 1. Scope and Application

This method outlines the procedure for determining surfactants in sea water. The method is applicable to sea water and effluent water which is free of the interferences listed below.

### 2. Principle of Method

In the presence of surfactants methyl green forms a blue complex. The complex is extracted with benzene and the intensity is measured on a spectrophotometer at 615 m $\mu$ . Beer's Law is obeyed to approximately 60  $\mu$ g in a 20 ml sample.

### 3. Interferences

No interferences have been found in sea water. Interferences which may be present in effluents include thiocyanate, nitrate, and nitrite. The interferences are reduced greatly, however, when using this method.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

- a. Separatory Funnels - 125 ml.
- b. Graduated Cylinders.
- c. Volumetric Flasks - 100 ml.
- d. Pipet - 2 ml.

### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

## 7. Reagents

a. Glycine Hydrochloride Buffer: Add glycine - HCl to 250 ml reagent water until a pH of 2.5 is reached.

b. Methyl Green, (0.5%): Dissolve 0.5 g methyl green in 100 ml reagent water.

c. Benzene - reagent grade.

d. Standard Surfactant Solution: Dissolve 1.000 g ABS (100 percent active) in 1 liter reagent water. Dilute 10 ml of this solution to 1 liter with reagent water. 1 ml of this solution contains .01 mg ABS.

## 8. Sampling

Samples shall be taken in clean plastic or glass bottles. Samples shall be at room temperature prior to beginning the analysis.

## 9. Calibration and Standardization

Prepare a series of standards ranging from 0.05 ppm to 3 ppm using the standard surfactant solution. Treat these standards as outlined under Procedure and plot a mg surfactants vs. absorbance curve.

## 10. Procedure

To a 20 ml sample in a separatory funnel, add 10 ml of glycine-HCl buffer (pH 2.5) and 2 ml 0.5% methyl green solution. Shake well and allow to stand 5 minutes. The dye complex is extracted with 40 ml benzene which is then further treated with 15 ml of glycine-HCl buffer. The benzene layer is then diluted to 100 ml with benzene and read at 615 m $\mu$  (maximum absorbance of the complex in benzene).

## 11. Calculations

Absorbance reading is determined by comparing sample with a benzene blank. Mg surfactants is obtained from standard curve prepared using known amounts of ABS. ppm is determined using the following equation:

$$\text{ppm surfactants} = \frac{\text{mg surfactants (from curve)} \times 1,000}{\text{ml sample}}$$

## 12. Precision and Accuracy

Results are reproducible to 0.05 ppm.

## SECTION 26. VOLATILE HYDROCARBONS IN SEA WATER

### 1. Scope and Application

This method outlines the procedure for determining volatile hydrocarbons in sea water. The method is applicable to sea water, effluent, and product water. Research and development work for this procedure was performed by Koppers Company, Inc., Research Division, Monroeville, Pennsylvania under contract (#14-01-001-204) to the Office of Saline Water.

### 2. Principle of Method

The aqueous solution to be analyzed is fed at a known rate into a gas stripping unit. The stripping gas is vented through the sample loop of a gas sampling valve of a hydrogen flame ionization detector. At intervals the valve is actuated to inject a sample of the stripper gas into the carrier gas stream of the detector unit. The output from the hydrogen flame ionization detector is amplified and recorded. The amount of hydrocarbon in the water is calculated from calibration curves prepared from data obtained with synthetic mixtures. The lower limit of detection is 0.05 ppm.

### 3. Interferences

No interferences have been found in sea water.

### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

### 5. Apparatus

a. Analytical unit for measurement of hydrocarbon content (Research Appliance Company, Allison Park, Pennsylvania. Constructed in accordance with the specifications of the Koppers Company, Inc., Research Department, Monroeville, Pennsylvania. A copy of the specifications can be found in R & D Report No. 115.) With proper selection of electrometer, detector, columns, etc., commercial gas chromatographs may be used. The instrument described may be used for on-line monitoring.

b. Copper Tubing, 1/4-inch O.D., 0.030-inch wall thickness, soft temper; 1/8-inch O.D., soft temper.

c. Glass Wool, Pyrex-brand.

d. Microliter Syringes, 0.5-, 1.0-, 5.0-, and 10.0-milliliter capacities with fixed needle and Teflon-tipped plunger.

e. Pressure-Reducing Regulators, two-stage, for use with compressed nitrogen, air, and hydrogen gases.

f. Pressure-Reducing Regulator, two-stage, for use with compressed standard butane-nitrogen mixture.

g. Vacuum Pump, oil-sealed, motor driven.

h. Sieve Screens, brass, U.S. Standard, 30- and 60-mesh sizes.

i. Soap Film Meter, calibrated from 0 to 50 ml.

j. Crystallizing Dish, Pyrex-brand glass, 150-mm. diameter.

k. Oven, thermostatted, gravity-convection type, suitable for use up to 125°C.

l. Filtering Flask, with side tube, Pyrex-brand glass, 1-liter capacity.

m. Gas Sample Bottle, 225-ml capacity, and Aqueous Solution Reservoir, 2000-ml capacity, of the same special design (see Drawing No. F-22611-V).

n. Leveling Bulb, 500-ml capacity.

o. Glass Sampling System, special design (see Drawing No. F-22611-V).

p. Stand-pipe, stainless steel.

q. Serum Stoppers, to fit side-arm of gas sample bottles.

r. Powder Funnel.

s. Swagelok Fittings, brass, for use with 1/4-inch O.D. copper tubing.

t. Stopwatch.

u. Swagelok Union, brass, for 1/8-inch copper tubing.

v. Polyurethane Tubing, 1/4-inch I.D., 1/16-inch wall thickness.

w. Tygon Tubing, 3/16-inch bore.

x. Graduated Cylinder, 100-ml capacity.

y. Stainless Steel Tank, 6-inch diameter by 24-inch length, 1/4-inch pipe thread opening each end.

z. Needle Valve, stainless steel, 1/4-inch pipe thread each end.

## 6. Purity of Reagents

Specifications for reagents are listed in Paragraph 7, Reagents.

## 7. Reagents

a. Acetone, technical-grade.

- b. Carbon Tetrachloride, technical-grade.
- c. Chloroform, reagent-grade.
- d. Molecular Sieve 5A, 1/16-inch pellets.
- e. Methylene Chloride, reagent-grade.
- f. Fluorosilicone QF 1-0065 G19.
- g. "CHROMOSORB P."
- h. Mercury, metal, distilled, technical-grade.
- i. Nitrogen, compressed, prepurified, 99.99 percent minimum purity.
- j. Hydrogen, compressed, prepurified, 99.9 percent minimum purity.
- k. Breathing Air, compressed.
- l. Gas Mixture, compressed, 100 ppm n-butane, instrument-grade, in nitrogen, prepurified, certified analysis.
- m. n-Butane, instrument-grade, 99.5 percent minimum purity.
- n. Stopcock Grease, high vacuum.

## 8. Sampling

Samples are taken in clean gas sample bottles or aqueous solution reservoirs described under Paragraph 5, Apparatus.

## 9. Procedure

### a. Preparation of Column

(1) Dissolve 5 grams of Fluorosilicone in about 100 ml of methylene chloride contained in a 150-mm-diameter crystallizing dish. Then add 45 grams of Chromosorb P to the solution and mix the slurry.

(2) Allow the major portion of the methylene chloride to evaporate by allowing the slurry to stand at room temperature. Swirl the contents of the crystallizing dish periodically to remix the slurry. Then remove the last traces of the solvent by drying the material for 2 hours in an oven at 120°C. Size the dried material through a 30- and on a 60-mesh screen.

(3) Cleanse thoroughly the inside surface of an 8-inch length of 1/4-inch O.D. by 3/16-inch I.D. copper tubing by rinsing it first with acetone, then with carbon tetrachloride, and finally with chloroform.

(4) Dry the tubing thoroughly by attaching it to a vacuum pump and aspirating air through it for about 30 minutes.

(5) Plug one end of the tubing with a small amount of glass wool. Pour the impregnated Chromosorb P slowly through a powder funnel into the other open end while tapping the tubing to insure uniform distribution of the packing. Close the packed tube with a small plug of glass wool.

(6) Bend the packed tube as necessary for installation in the column compartment of the detector unit.

(7) Attach Swagelok fittings to both ends of the tube.

b. Preparation of Apparatus

(1) Attach the gas supplied to the inlets of the Conoflow regulators. The hydrogen cylinder should be independently well grounded.

(2) Install the packed tube in the column compartment of the detector unit.

(3) Turn all switches on the panels of the analyzer unit to the off position.

(4) Connect the power cable to the connector at the bottom rear of the unit. Plug the other end into a 110-volt a.c. 60-cycle source. Be sure the analyzer unit is well grounded.

(5) Throw on the master power circuit breaker on the flame ionization detector panel.

(6) Adjust the block heater variable transformer to a setting of 30 to obtain a detector block temperature of  $110^{\circ}\text{C}$ . Throw the block heater switch to the on position.

(7) Throw the electrometer switch to the warm-up position. Leave it there for at least 10 minutes, then throw it quickly to the operate position. ALLOW AT LEAST FOUR HOURS FOR ELECTROMETER STABILIZATION BEFORE OPERATING.

(8) Install the chart as described in Section 352-1 of the recorder instruction manual.

(9) Fill and start the pen as described in Section 354-2 of the recorder instruction manual.

(10) Turn on the recorder power switch to energize the amplifier. ALLOW AT LEAST 30 MINUTES FOR AMPLIFIER WARM-UP.

(11) Adjust the zero controls as described in Section 634-6b of the recorder instruction manual. The electrometer range is set at 10,000 and the attenuator at  $\infty$  for this adjustment.

(12) Several minutes after performing step 5, turn the temperature selector switch to the detector position. A deflection of 18 chart divisions will indicate a detector block temperature of 110°C. Readjustment of the block heater variable transformer may be necessary to achieve this temperature.

(13) With the packed column in position and the oven cover in place, turn on the blower switch.

(14) Turn on the air, nitrogen and hydrogen supplies and with the Cono-flow regulators adjust the gas flows as listed in Table 1. Flowrator settings are read at the top of the ball.

TABLE I  
APPROXIMATE GAS FLOW ADJUSTMENTS

<u>Gas</u>	<u>Cylinder Pressure</u> psi.	<u>Flowrator Setting</u>	<u>Flow</u> ml/min.
Hydrogen	30	8.70	40
Nitrogen carrier	40	13.35	80
Air	30	5.00*	275

\*Setting to obtain a flow of 275 ml/min. varies depending on the back pressure adjustment of the needle valve after the Conoflow regulator.

(15) Rotate the meter relay adjusting knob counterclockwise until the red arm reads 0°C on the flame temperature meter. The black needle will read near the temperature of the cell. Remember this black needle reading for step 17.

(16) Turn on the igniter switch. Push the manual igniter button in and hold for several seconds. The black needle of the meter relay will go upscale. Determine if the flame is lit by removing the cell cover and putting a thin strip of paper down into the cell, over the jet. The normal flame is not visible. If the flame will not light, observe the igniter button. The wire should glow red within two seconds if properly adjusted.

(17) After the flame is lit, adjust the red arm of the meter relay to a value less than the temperature now indicated by the black needle, but above the cell temperature as measured in step 15. (The temperature of the thermocouple should go up by about 100°C on igniting the flame. If it does not, move the thermocouple closer to the flame.)

(18) Set the electrometer range at 10,000 and the attenuator at 8. With the coarse control knob and the fine control knob, adjust the recorder chart drive by setting the hour timer at zero, the minute timer at 15, and turning on the power switch located on the panel beneath the timers.

(19) After allowing sufficient time for complete equilibrium of the detector, the unit is ready for adjustment to the standard gas response.

(20) Follow the instruction manuals furnished by the manufacturers of the detector, recorder, and pump for details of operation and recommended maintenance.

### c. Adjustment of Standard Gas Response

(1) Attach the standard n-butane-nitrogen supply to the inlet of the Cono-flow regulator.

(2) Close the needle valve in the gas line from the stripper to the gas sample loop to prevent standard gas flow through the stripper. This valve is located inside the rear door of the analyzer cabinet.

(3) Adjust the Conoflow regulator and needle valve in the standard gas line to provide a flow of 50 ml per minute through the gas sample loop. Use the soap film meter for this measurement.

(4) Set the electrometer range at 100 and the attenuator at 2 and adjust the recorder pen to the zero mark.

(5) Turn on the power switch beneath the timers and set the hour timer at 2 hours. (The pump and stripper may be unplugged during the remainder of this adjustment.)

(6) Throw the manual test sample switch and hold for one minute, then release.

(7) Repeat step 6 at 2-minute intervals for replicate analyses of the standard gas.

(8) The average of four analyses should be within  $\pm 1.0$  chart division of the response for the n-butane concentration of the standard gas from the calibration curve (Note 1).

(9) Minor flow adjustments of the nitrogen carrier and hydrogen gas flows may be required to obtain the desired response value. If flow changes are made, 10 to 15 minutes should be allowed for stabilization before repeating steps 6 through 8.

(10) After the desired response value is obtained, wait 15 minutes and repeat steps 6 through 8 to be certain that stabilization of gas flows has been achieved (Note 2).

(11) Turn off the standard gas supply and open the needle valve in the gas line from the stripper to gas sample loop.

(12) The analyzer is now ready for analysis of samples.

d. Calibration (Note 1)

(1) Fill a calibrated gas sample bottle containing 1 ml of mercury with air or nitrogen to atmospheric pressure.

(2) Using the appropriate gas-tight syringe, inject a measured volume of n-butane through the serum stopper in the side arm of the bottle.

(3) Mix the gases by turning the bottle end-over-end for several minutes.

(4) Connect the bottle to the mercury leveling bulb and the injection system shown in Drawing No. F-22611-V.

(5) Using this system, evacuate the sample loop and fill it to atmospheric pressure with the synthetic mixture.

(6) Inject the sample with the manual test sample switch.

(7) Adjust the electrometer range setting for the n-butane concentration range of interest, and attenuate the recorder range as necessary to keep the peak within the limit of the chart paper.

(8) Repeat steps 5 through 7 for replicate analyses of the same synthetic mixture.

(9) Repeat steps 1 through 8 with several mixtures over the concentration range of interest (Note 3).

(10) Prepare a calibration curve by plotting response in chart divisions versus n-butane concentration (Note 4). See Graphs 1 and 2 for examples.

(11) The instrument may be calibrated using other gases. Examples of calibration curves using various gases are shown in Figures 1 through 19.

e. Sample Calibration

(1) Fill a calibrated gas sample bottle of 222.6 ml volume containing 1 ml of mercury with nitrogen to atmospheric pressure.

(2) Using the 10 ml gas-tight syringe, inject 5.90 ml of n-butane through the serum stopper in the side arm of the bottle. The syringe should be flushed twice with n-butane before the final filling to 5.90 ml with n-butane.

(3) Mix the gases by turning the bottle end-over-end for several minutes.

(4) Fill a second calibrated gas sample bottle of 217.0 ml volume containing 1 ml of mercury with nitrogen to atmospheric pressure.

(5) Using the 1 ml gas-tight syringe, inject 0.20 ml of the mixture prepared in step 3 through the serum stopper in the side arm of the bottle. The syringe should be flushed twice with the gas mixture before the final filling to 0.20 ml with the mixture.

(6) Mix the gases by turning the bottle end-over-end for several minutes.

(7) With the electrometer range setting at 100 and the recorder range attenuator at 2, follow steps 4 through 8 of the Calibration section to obtain the response in chart divisions.

(8) Repeat steps 4 through 7 with several mixtures over the concentration range of interest. Examples are listed in Table II.

(9) The gas mixture prepared in step 3 should be maintained at atmospheric pressure by replacing the gas removed from the sample bottle with mercury. This is accomplished by connecting a mercury leveling bulb to the sample bottle and maintaining equal levels of mercury in both the leveling bulb and the sample bottle.

TABLE II  
SAMPLE CALIBRATION MIXTURES

<u>Volume of Nitrogen</u> ml	<u>Volume of Gas Mixture From Step 3</u>	<u>n-Butane Concentration</u> ppm by Volume	<u>Electrometer Setting</u>	<u>Recorder Range Attenuation</u>
216.0	0.20	24	100	2
216.0	0.80	95	100	2
216.0	1.60	191	100	2
216.0	1.60	191	100	16
216.0	4.50	529	100	16
216.0	7.80	903	100	16

f. Analysis of Sample

(1) Fill the solution reservoir with distilled water and connect it to the Sigmamotor pump by means of 1/4-inch O.D. copper tubing. Use an 8-inch length of polyurethane tubing through the pump head. Use short (ca. 2 inches) sections of Tygon tubing to connect the reservoir and the stripper unit to the copper tubing. Flexible tubing can be used for the stripper exit line.

(2) Check to see that the standard gas supply is off and the needle valve in the gas line from the stripper to the gas sample loop is opened.

(3) Turn on the power switch beneath the timers to operate the pump and the stripper. Open the needle valves of the solution reservoir.

(4) Pump the water into the stripper unit until the water level is at the halfway point in the stripper, and adjust the standpipe to maintain this level.

(5) Adjust the pump rate to 50 ml per minute. Use a graduated cylinder to measure the volume pumped per minute from the stripper exit line. This adjustment is made on the vernier of the Sigmamotor pump.

(6) Adjust the Conoflow regulator and needle valve in the nitrogen stripping gas line to provide a flow rate of 50 ml per minute. Use the soap film meter for this measurement.

(7) Set the electrometer range at 100 and the recorder range attenuation at 2.

(8) After 5 to 10 minutes of operation, throw the manual test sample switch and hold for one minute, then release. The trace hydrocarbon peak from ordinary laboratory distilled water should not exceed one chart division (Note 5).

(9) Turn off the power switch beneath the timers and remove the distilled water reservoir (Note 6).

(10) Fill the reservoir with the sample solution to be analyzed and connect it to the pump.

(11) Open the needle valves and turn on the power switch (Note 7).

(12) Allow the system to operate for 5 to 10 minutes before throwing the test sample switch to inject a sample of the stripping gas into the detector unit.

(13) Repeat the analysis of the stripping gas at intervals of 2 to 4 minutes. Equilibrium will be attained in 10 to 15 minutes as indicated by duplicate peaks being recorded on the chart.

(14) Adjust the electrometer range setting and recorder range attenuation to keep the peak on the chart paper and according to those used for the calibration curve for the particular range of concentration.

(15) Calculate the n-butane content of the solution as described under Calculations.

NOTE 1 - The standard gas mixture used to obtain the calibration curve attached to this method contained 152 ppm by volume n-butane and gave a response of  $75.5 \pm 1.0$  chart divisions. It is recommended that a new supply of standard gas mixture be on hand before the original mixture is depleted. The new mixture should be analyzed with

the instrument adjusted to the response of the original mixture. This will avoid the preparation of new calibration curves.

NOTE 2 - If any adjustments of air, hydrogen or nitrogen gas flows are subsequently made, the standard gas response must be checked before analysis of samples.

NOTE 3 - For low concentrations (0-200 ppm), prepare a preliminary synthetic mixture of about 2 percent by volume of n-butane. From this mixture prepare blends of the required concentrations using the gas-tight hypodermic syringes.

NOTE 4 - If the detector unit is used under continuous operation, the standard gas mixture is analyzed at the beginning of each day's runs, and slight flow adjustments may be necessary to obtain the response shown on the calibration curve.

NOTE 5 - Should a solution of high hydrocarbon content have been run just prior to this analysis, the addition of 1 to 2 liters of distilled water may be necessary to completely purge the stripper unit and the lines.

NOTE 6 - The distilled water purging is necessary only for adjustment of water and stripper nitrogen flow rates when an insufficient quantity of sample is available for these adjustments and subsequent analysis.

NOTE 7 - When this analysis is to be made on a plant stream, connect the water stream to the pump, turn on the power switch, adjust the timers for frequency of sampling, and allow the system to purge until duplicate peaks are recorded.

## 10. Calculations

- a. Measure the peak height of the n-butane band in chart divisions.
- b. From the calibration curves previously prepared find the concentration of n-butane in the stripping gas sample analyzed in ppm by volume.
- c. From the ppm by volume in the stripping gas, calculate the ppm by weight in the solution as follows:

$$\frac{\text{ppm by volume in gas} \times 0.05}{E} = \text{ppm by weight in water}$$

where E = ppm by volume in stripping gas equivalent to 0.05 ppm by weight in water for n-butane.

This equivalent is calculated as follows:

0.05 ppm by weight in water

$$= \frac{5 \times 10^{-6} \times 10^{-2} \times W \times (22400 \times \frac{760}{P} \times \frac{273+t}{273}) \times 100}{M.W. \times V} \quad \begin{array}{l} \text{volume percent} \\ \text{in stripping gas} \end{array}$$

where W = weight of water stripped per minute, expressed in grams;

V = volume of stripping gas used per minute, expressed in milliliters;

P = barometric pressure, expressed in mm. of mercury;

t = ambient temperature, °C;

and M.W. = molecular weight of n-butane.

#### Sample Calculations

Barometric pressure = 740 mm.

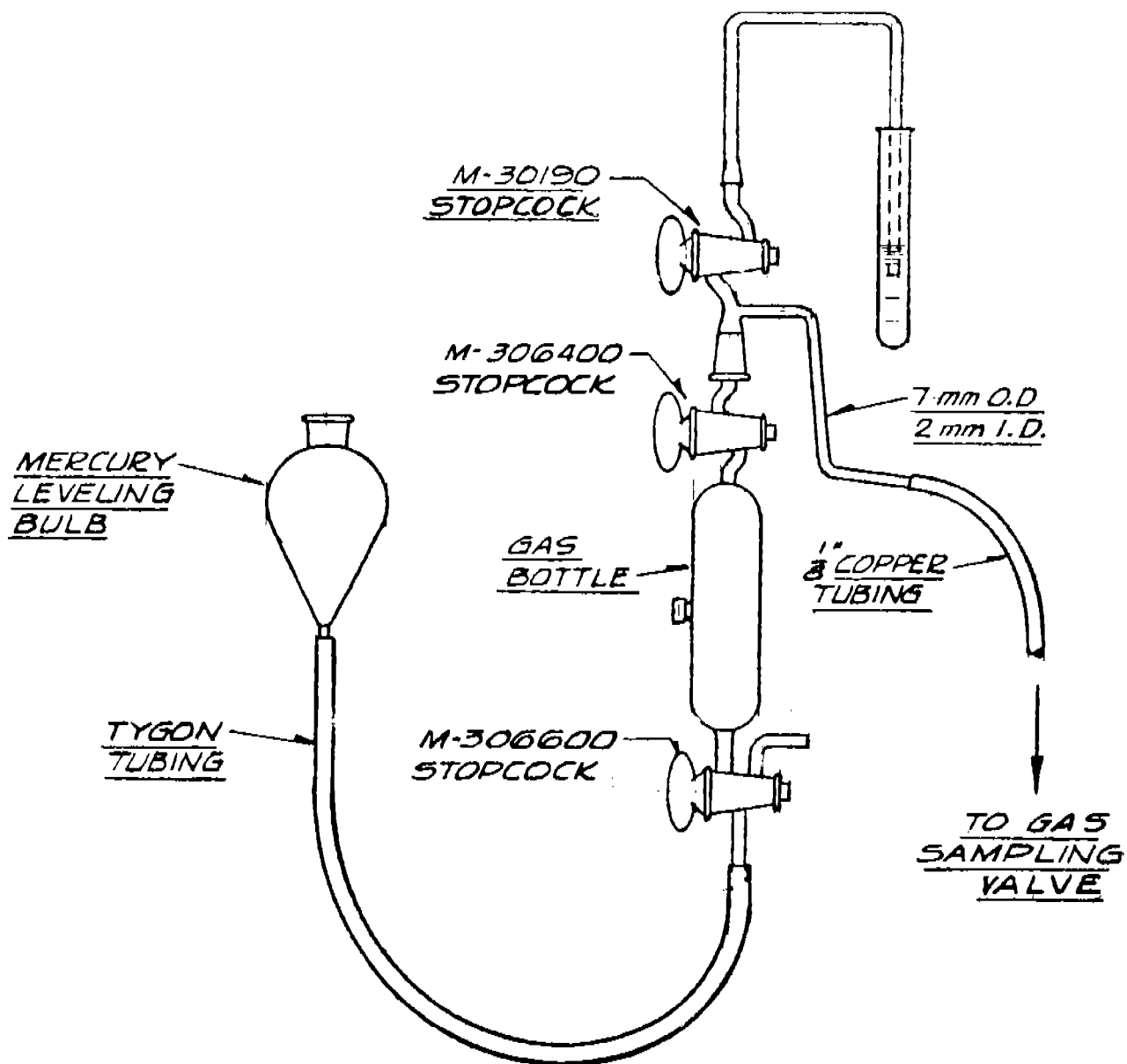
Ambient temperature = 23°C

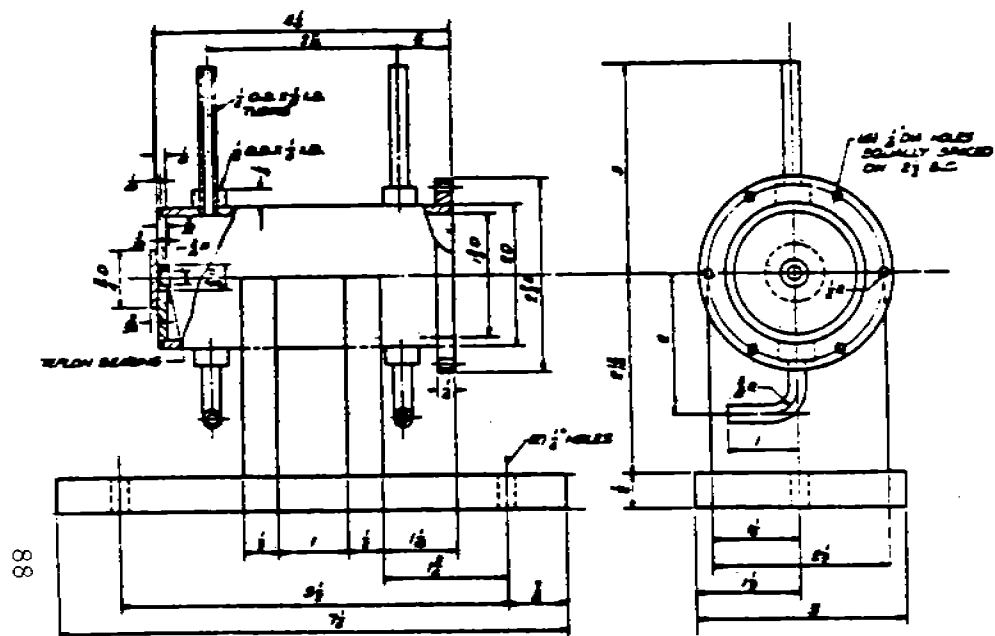
1:1 stripping rate

$$\begin{aligned} \text{En-butane} &= \frac{5 \times 10^{-8} \times 2.51 \times 10^6}{58} \text{ volume percent in gas} \\ &= 0.00216 \times 10^4 \text{ ppm by volume in the gas} \\ &= 21.6 \text{ ppm by volume} \end{aligned}$$

#### 11. Precision and Accuracy

The stripping efficiency of the unit was found to be 98 percent minimum. The reproducibility of the analysis at the lowest concentration studied is better than ± 5 percent of the amount present, and at the highest concentrations, it is better than ± 2 percent of the amount present.



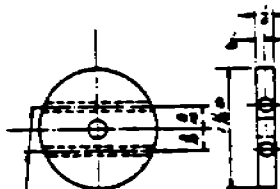


NOTE: ALL JOINTS TO BE SOLVENT WELDED

**MARK A**  
**BODY & BASE**  
MTRL: LUCITE EXCEPT  
AS NOTED

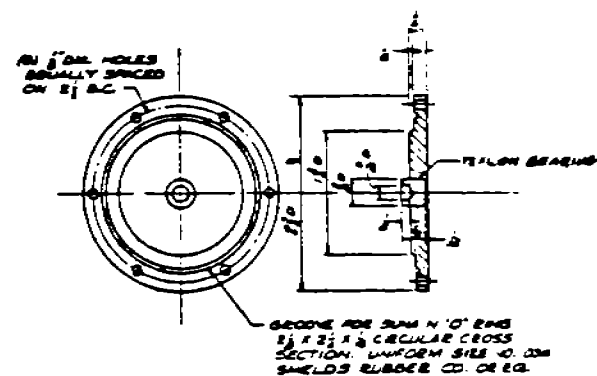


**MARK C**  
**SHAFT**  
MTRL: STEEL



DRAW 1/8" DIA HOLES  
INSERT SOFT IRON  
RODS & SEAL ENDS  
WITH LUCITE CEMENT

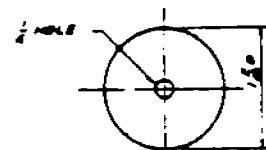
**MARK D**  
**DRIVE WHEEL**  
MTRL: LUCITE



**MARK B**  
**COVER**  
MTRL: LUCITE EXCEPT  
AS NOTED

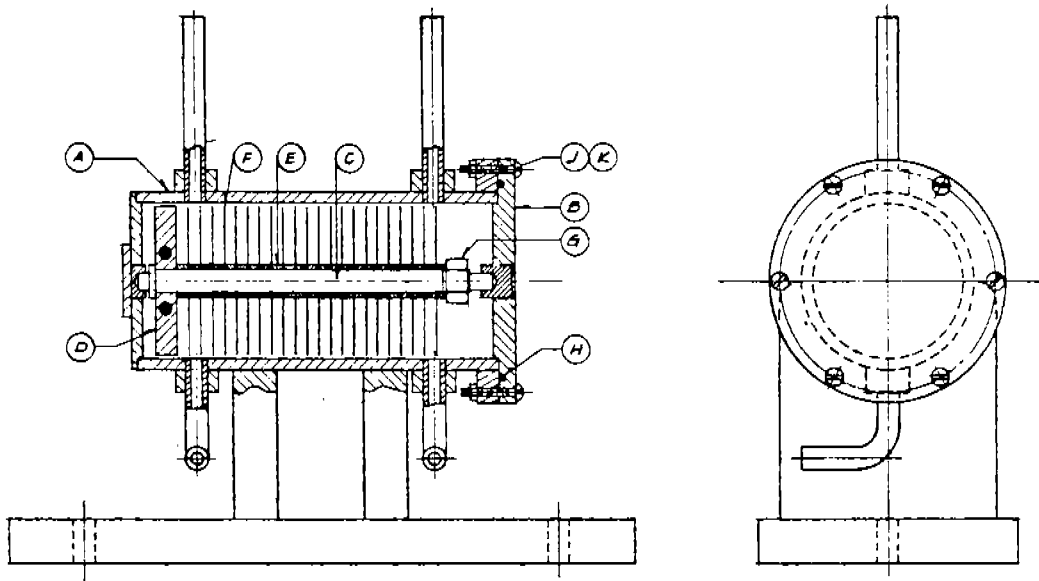


**MARK E**  
**SPACER**  
MTRL: LUCITE

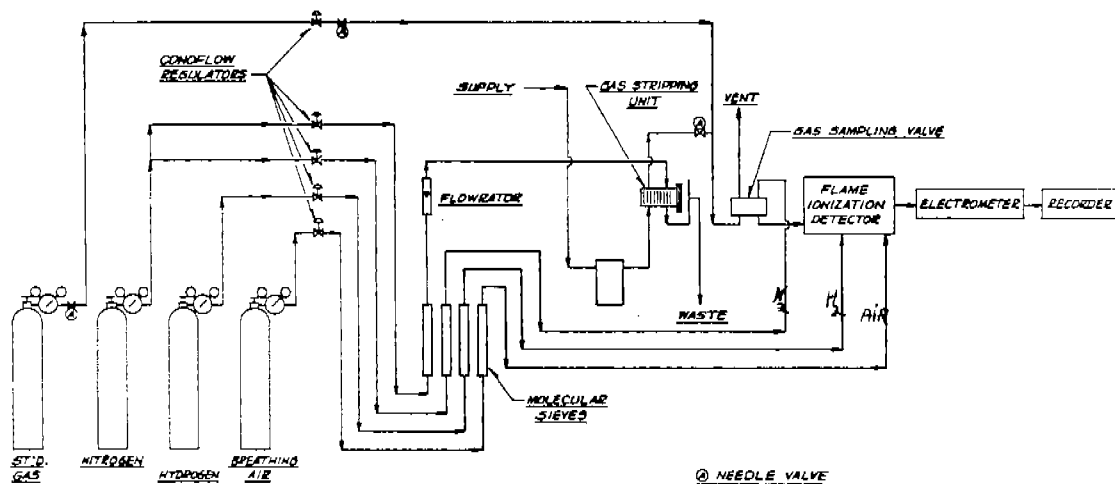


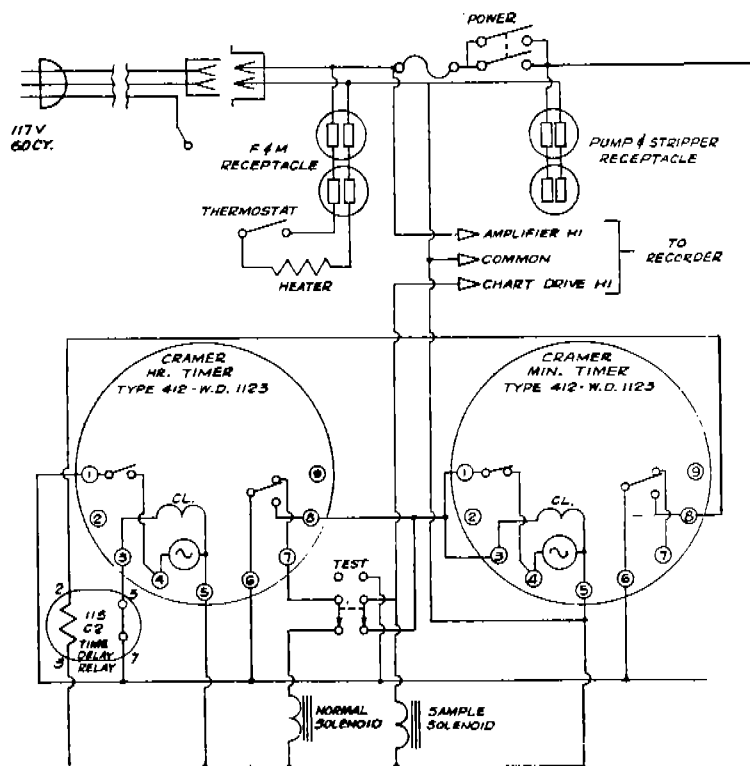
**MARK F**  
**DISC**  
MTRL: NYLON  
1/8" THICK

FOR ASSEMBLY SEE DWG. C-66713-V

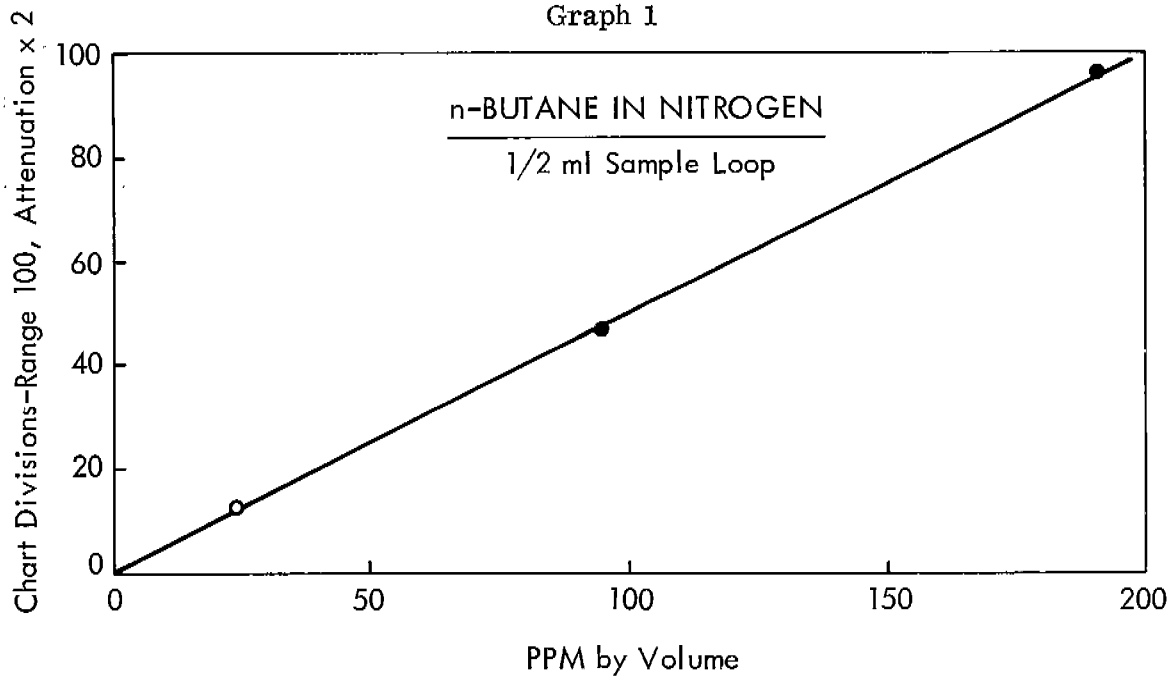


F	22	DISC	B-511123-V				
E	23	SPACER	B-511123-V				
D	1	DRIVE WHEEL	B-511123-V	K	6	F4-40 HEX HD NUT	
C	1	SHAFT	B-511123-V	J	6	#4-40 X 3/8 LG RD HDMS	
B	1	COVER	B-511123-V	H	1	O RING	
A	1	BODY & BASE	B-511123-V	G	1	TEFLON NUT 1/4-20	
ITEM	NO. REQ.	DESCRIPTION	DWG. NO.	ITEM	NO. REQ.	DESCRIPTION	DWG. NO.





Graph 1



Graph 2

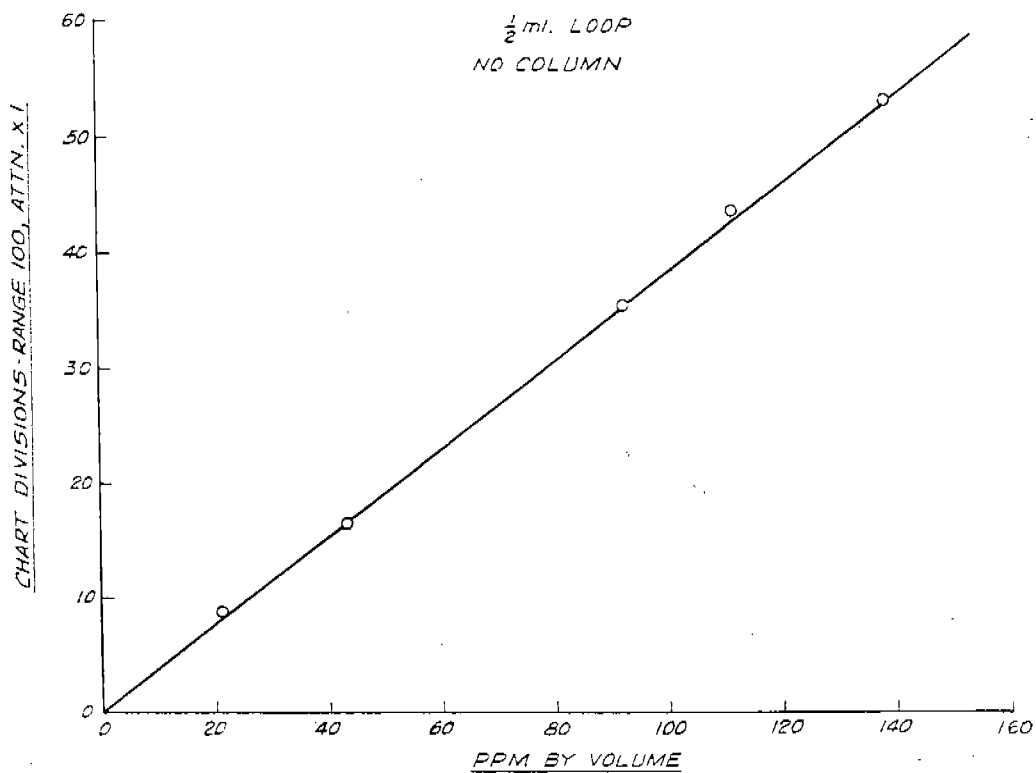
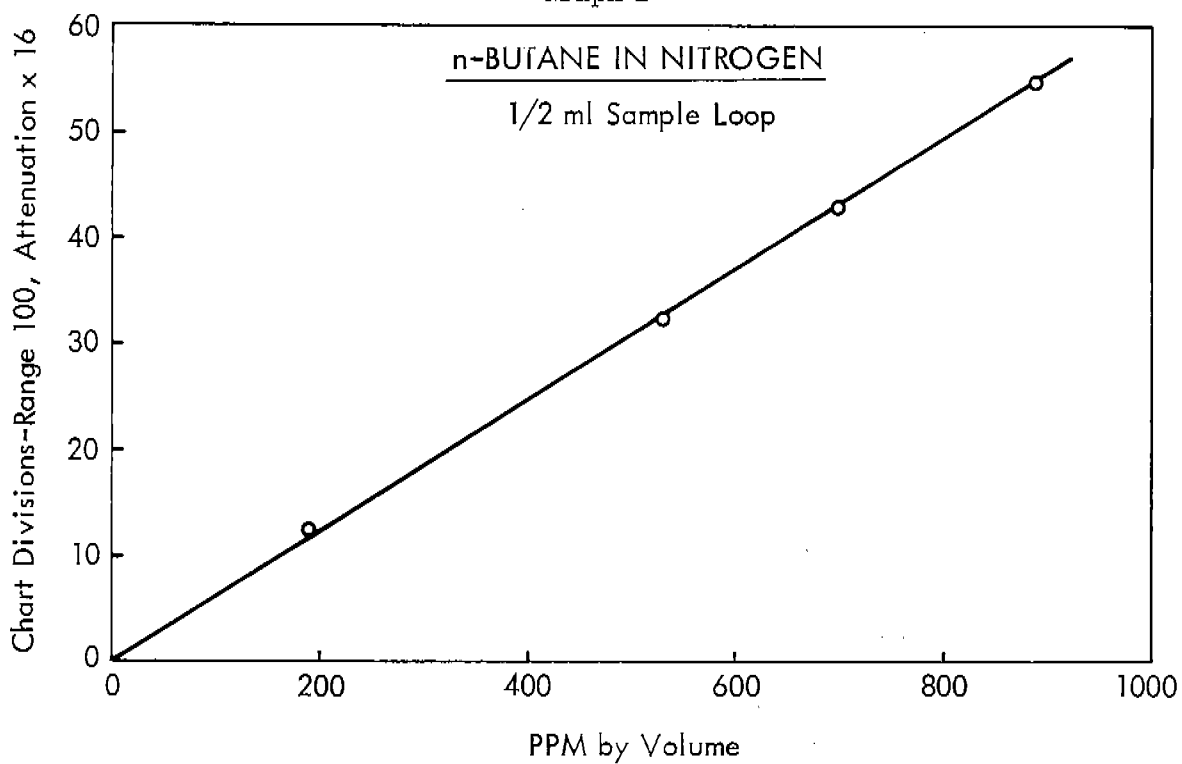


Figure 1. Propane in Nitrogen

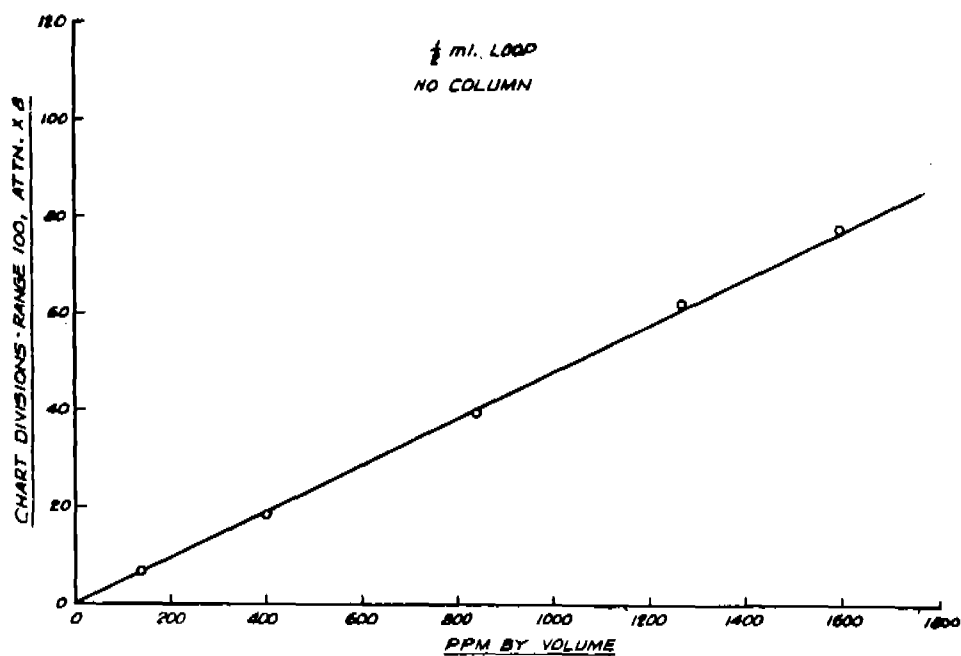


Figure 2. Propane in Nitrogen

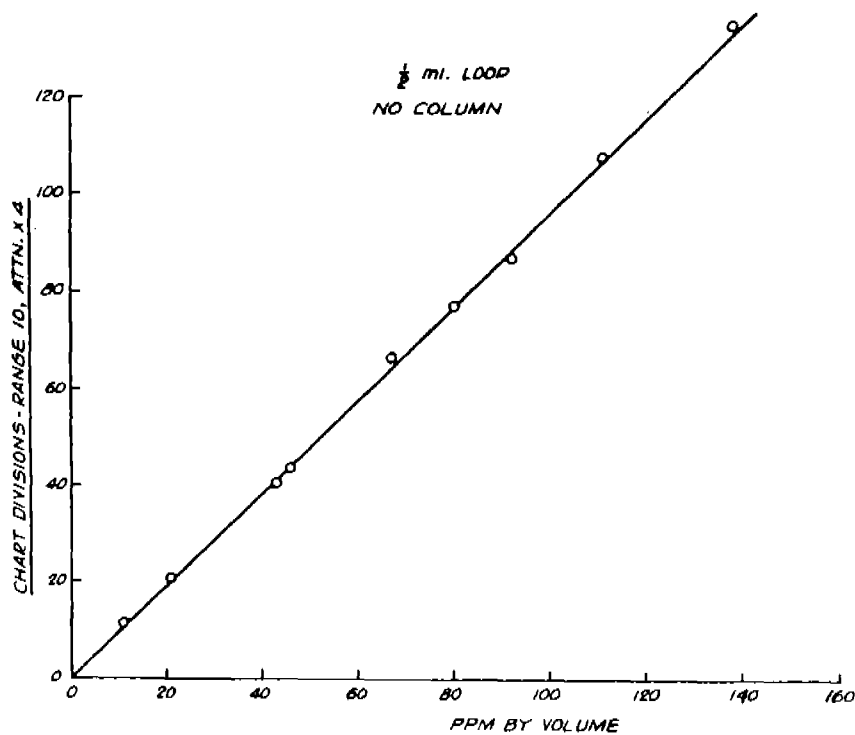


Figure 3. Propane in Nitrogen

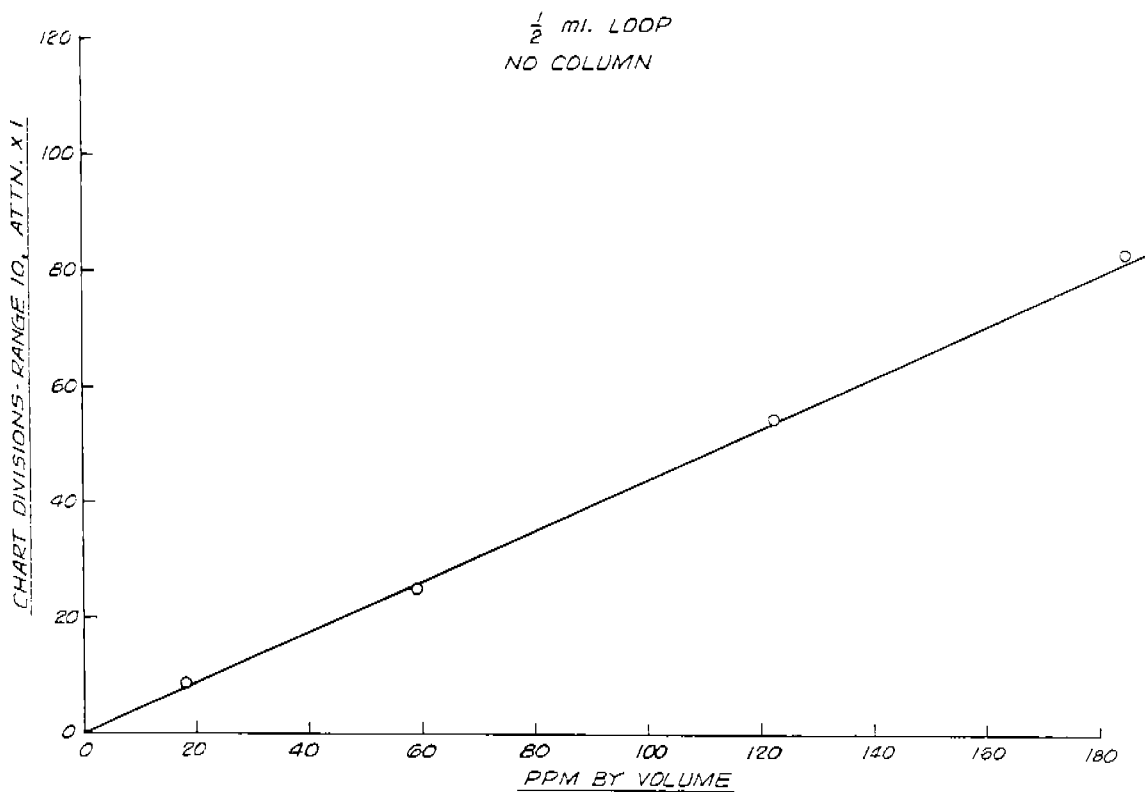


Figure 4. Freon-12 in Nitrogen

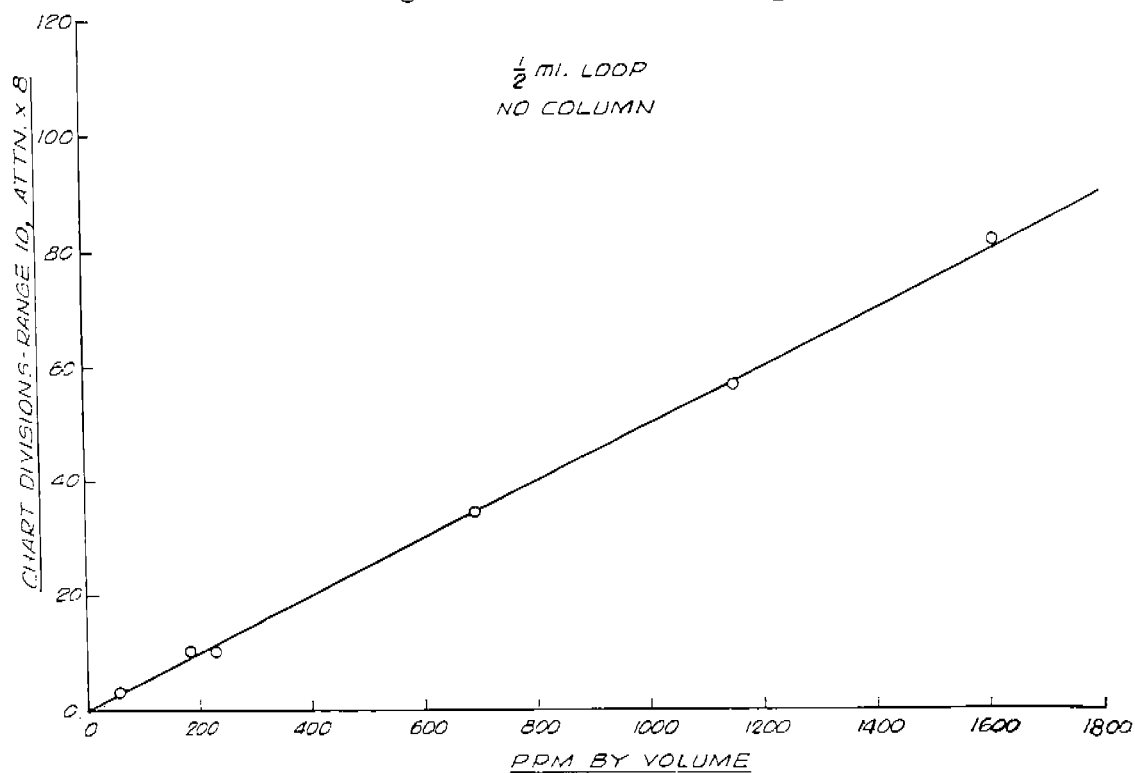


Figure 5. Freon-12 in Nitrogen

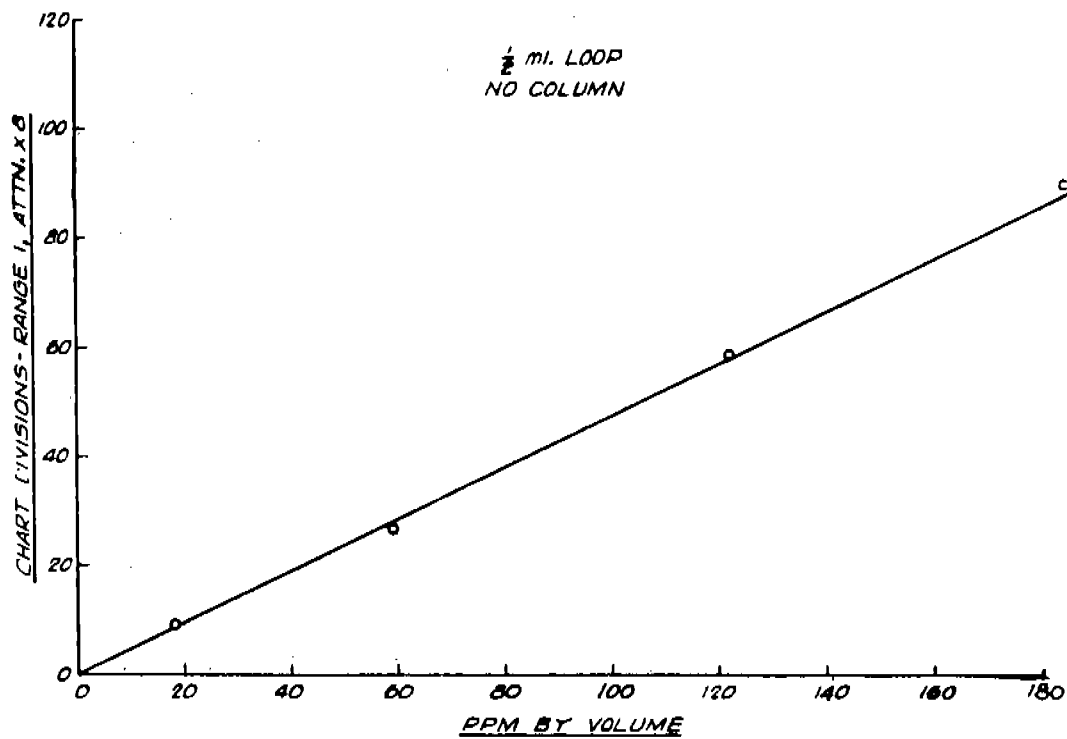


Figure 6. Freon-12 in Nitrogen

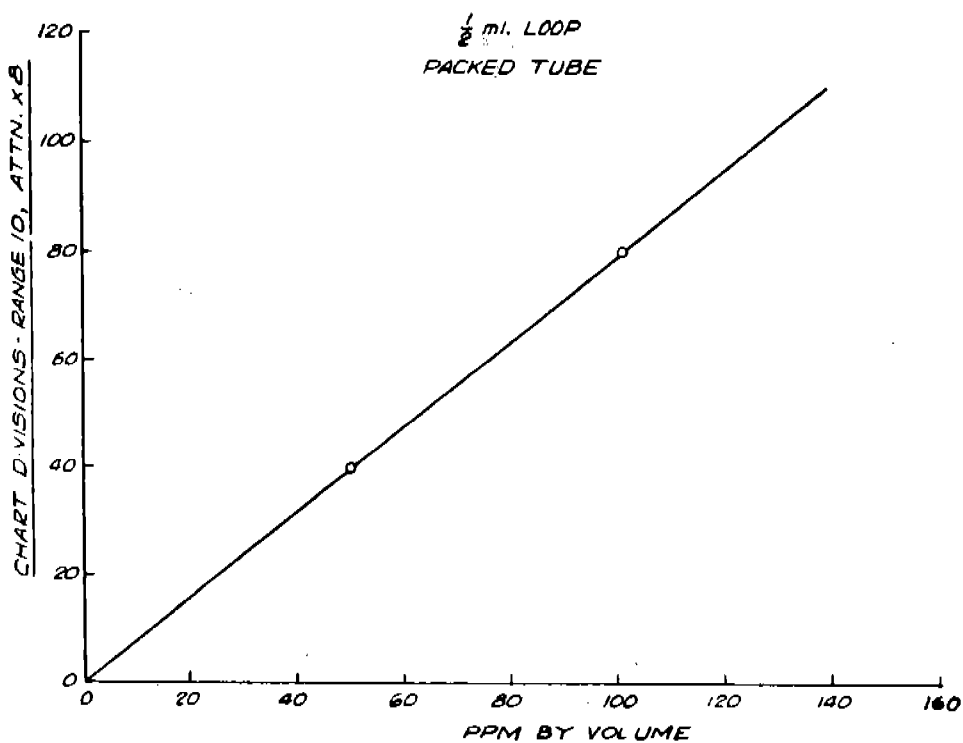


Figure 7. Propane in Nitrogen

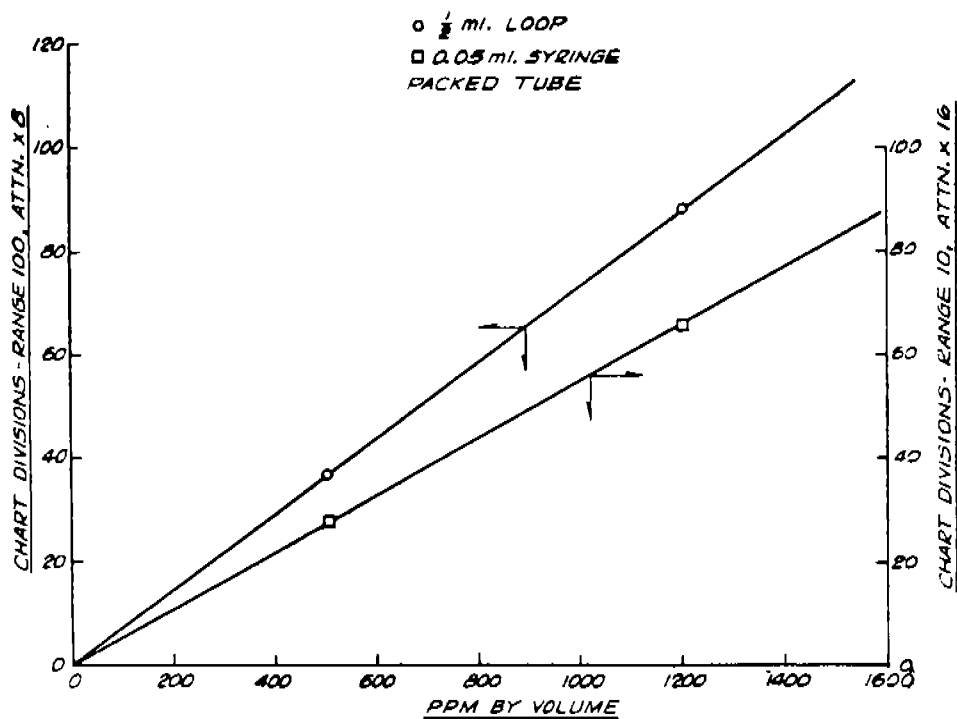


Figure 8. Propane in Nitrogen

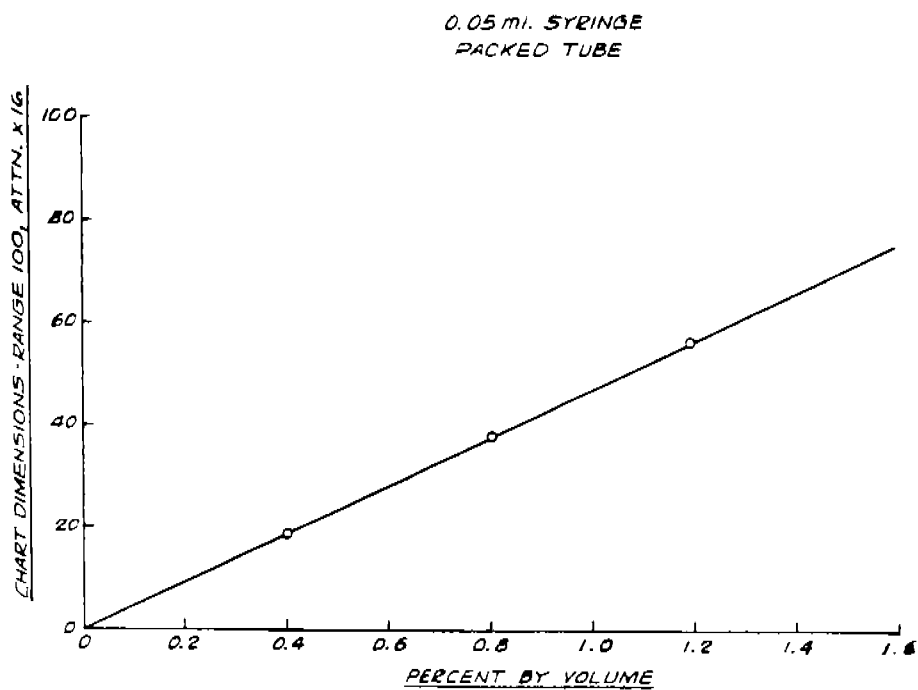


Figure 9. Propane in Air

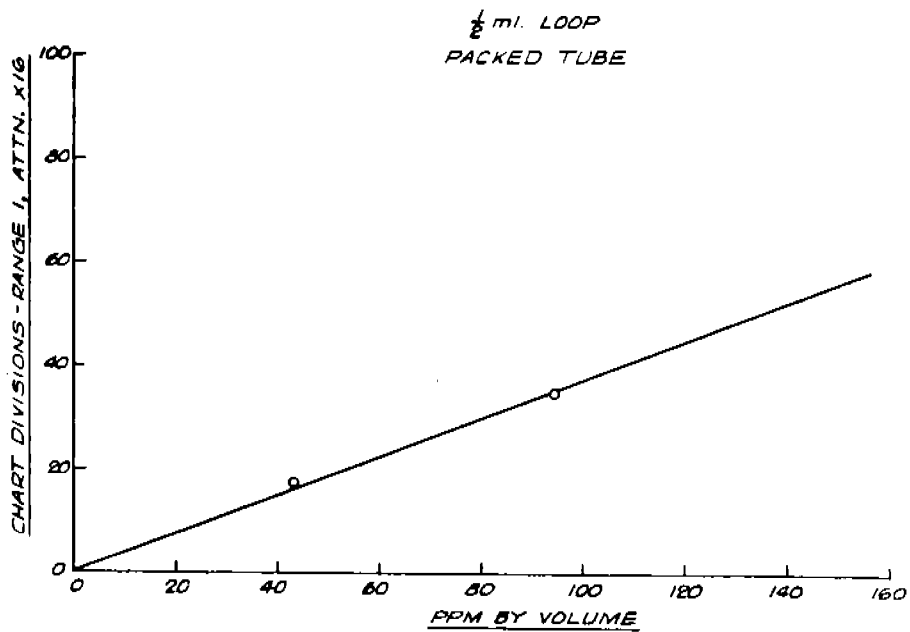


Figure 10. Freon-12 in Air

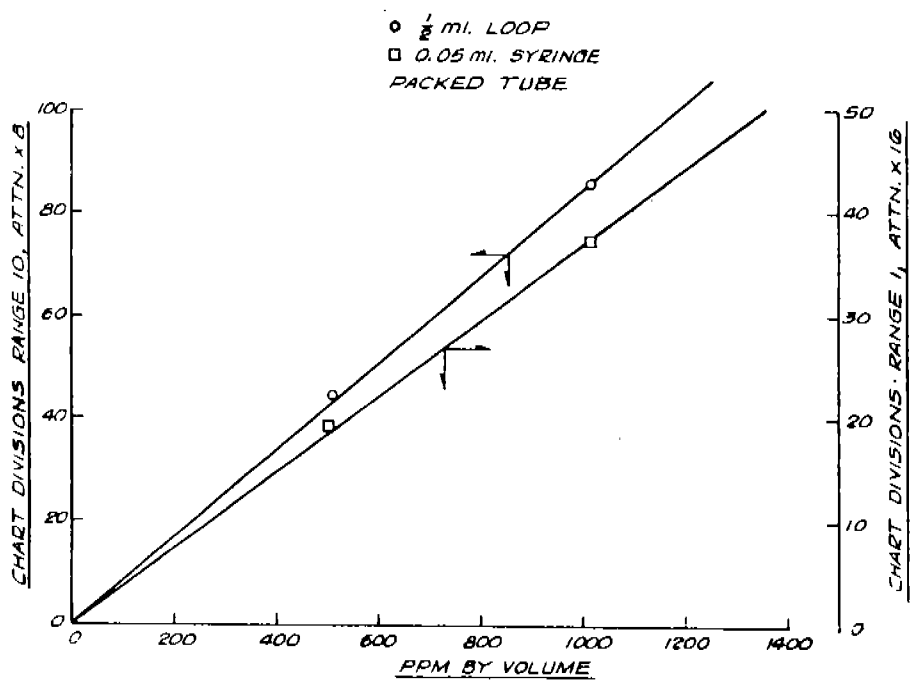


Figure 11. Freon-12 in Air

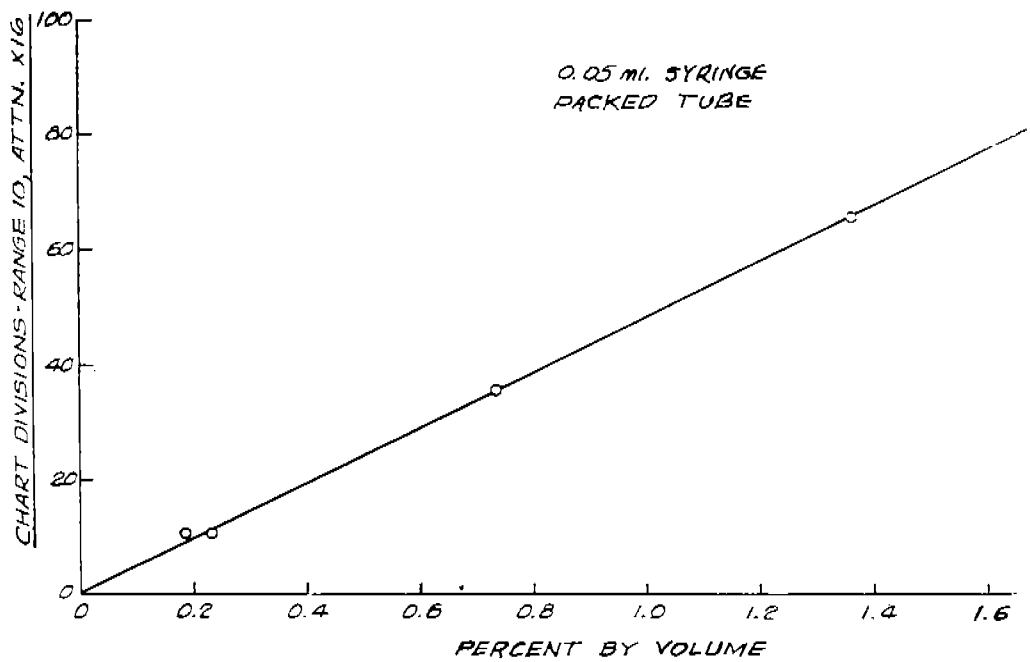


Figure 12. Freon-12 in Air

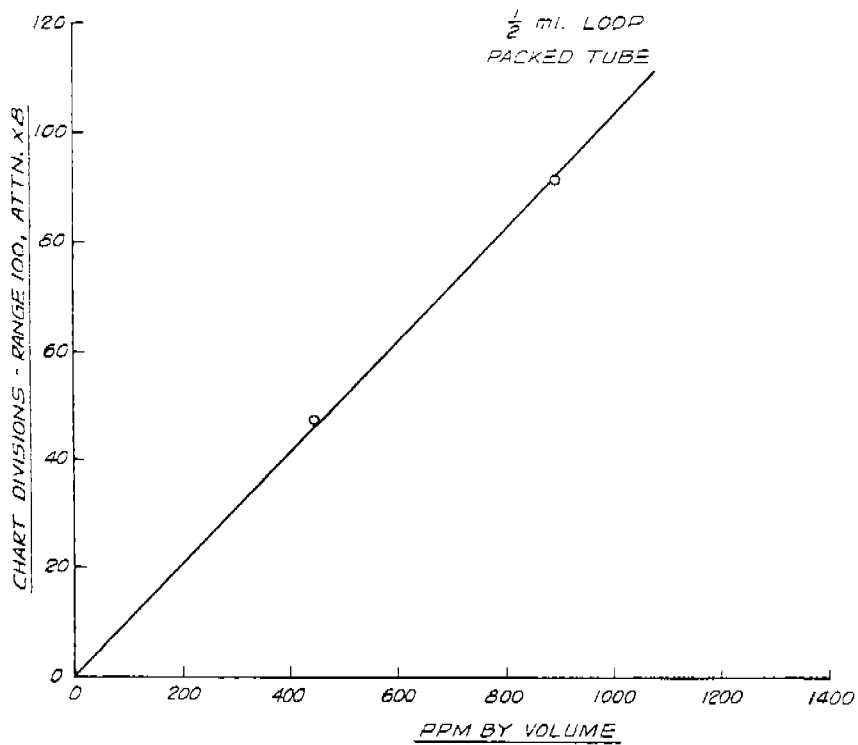


Figure 13. Isobutane in Air

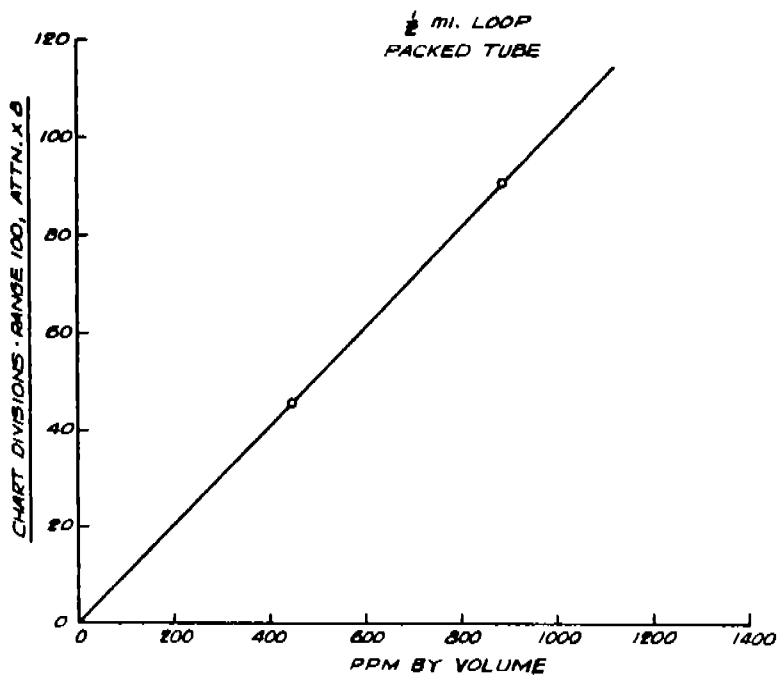


Figure 14. n-Butane in Air

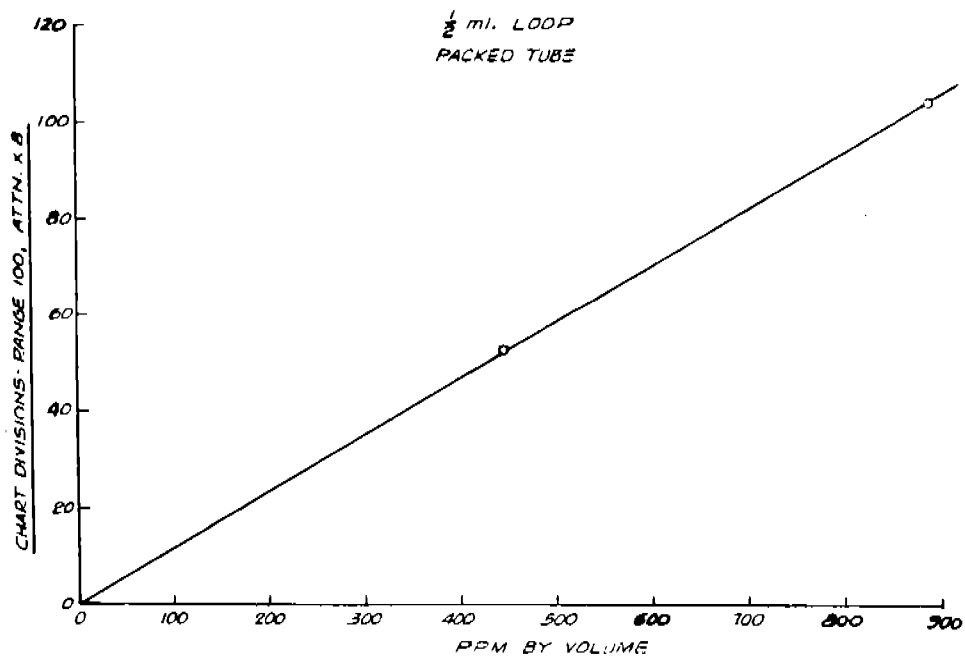


Figure 15. Butene-1 in Air

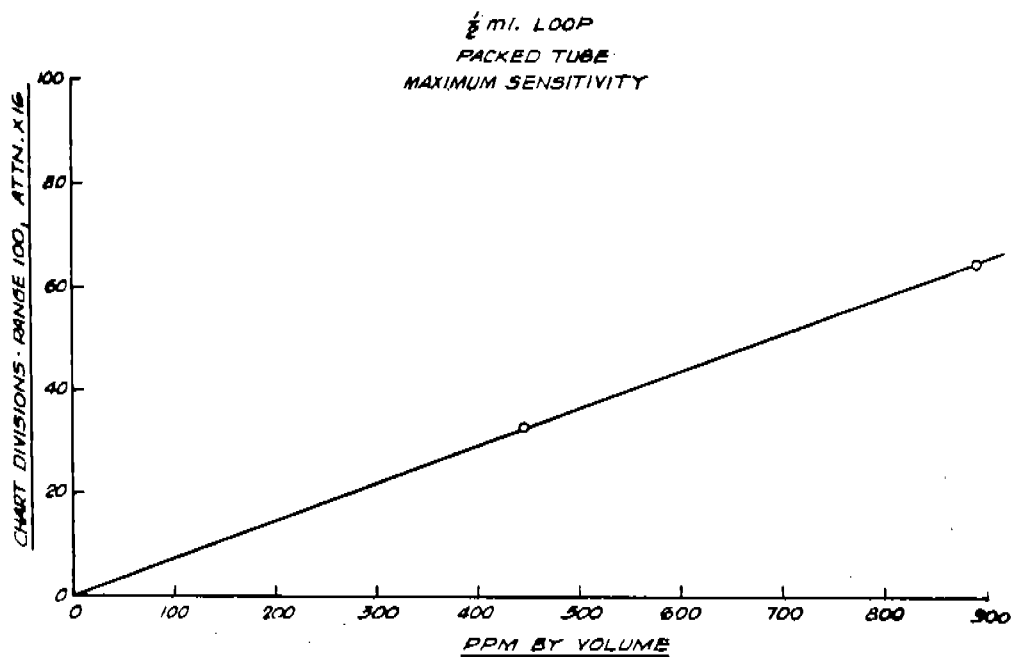


Figure 16. Propane in Air

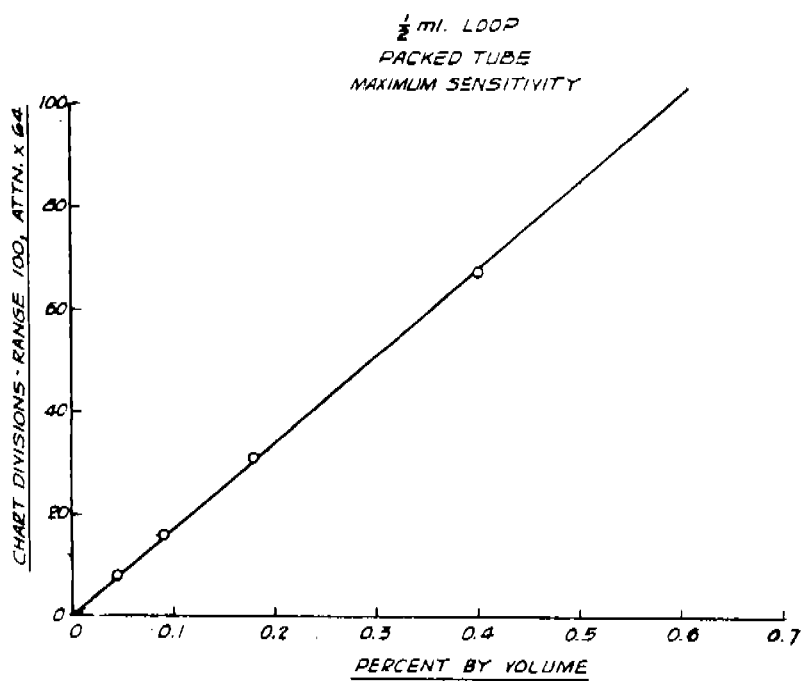


Figure 17. Propane in Air

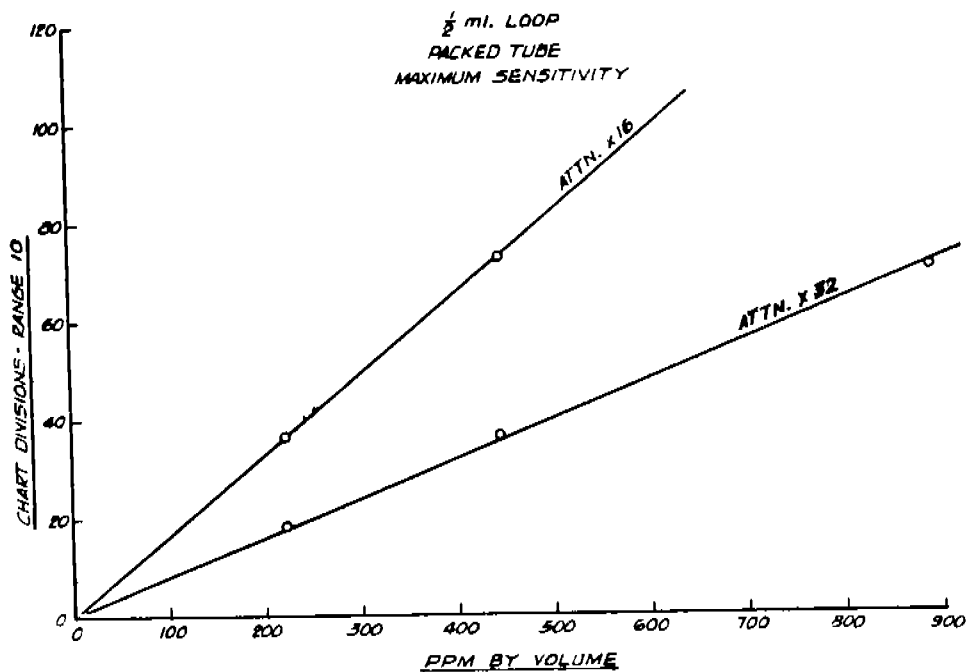


Figure 18. Freon-12 in Air

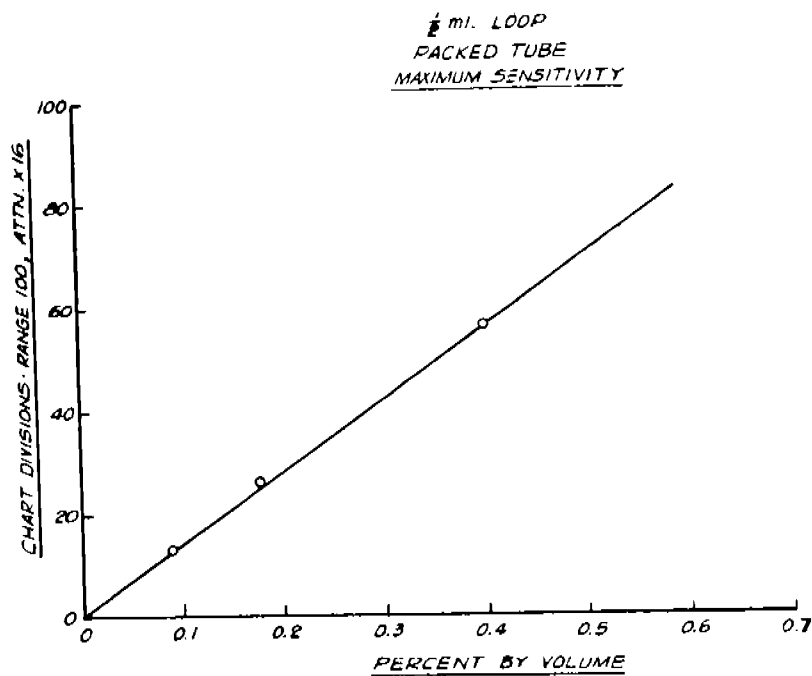


Figure 19. Freon-12 in Air

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## CHAPTER II. ANALYTICAL PROCEDURES FOR SCALE

## SECTION 1. INTRODUCTION

This section is devoted to analytical procedures which have been found applicable to scale and water formed deposits. Research and development work was conducted at the Office of Saline Water's Research and Development Test Station at Wrightsville Beach, North Carolina. Methods were evaluated and modified, if necessary, until satisfactory procedures were obtained. The methods outlined include colorimetric, gravimetric, titrimetric, and instrumental methods of analysis. New methods of analysis, such as atomic absorption spectroscopy, will be added as they are developed.

## SECTION 2. REPORTING RESULTS

### 1. Scope

This section outlines items which shall be included, if available, when reporting results obtained by methods covered in this manual.

### 2. Items to be Reported

#### a. Sample Identification

- (1) Name of Contractor
- (2) Contractor sample identification
- (3) Plant conditions
- (4) Date sample taken
- (5) Analyses to be made
- (6) Date results needed

#### b. Laboratory Identification

- (1) Lab test number
- (2) Date submitted
- (3) Date analyses began
- (4) Date analyses completed
- (5) Man-hours required
- (6) Cost of special apparatus and/or chemicals
- (7) Analyst reporting results

### c. Test Results

Results are expressed as outlined under the Calculations paragraph of each method. The form used to report results shall be left to the discretion of the individual laboratory. Generally, in scale analyses, the report should include the percentage of the original amount of sample accounted for. The analyst should attempt to account for at least 90 percent of the sample by analysis. Conversion of iron, copper, calcium, magnesium, carbonate, etc., to expected compounds as indicated by the analysis is required.

## SECTION 3. PREPARATION AND ANALYSIS OF SCALE

### 1. Scope and Application

This method outlines the preparation of solid materials which are to be analyzed. The method is applicable to scales or water formed deposits.

### 2. Principle of Method

The solution of the scale is generally effected by using a mixture of mineral acids, hydrochloric, nitric, and perchloric. Certain silicate complexes may not be dissolved by this method but will be broken down by further treatment with hydrofluoric acid and sodium carbonate. The complexes may include sodium, potassium, tin, and some phosphate if present in the original sample. With the carbonate fusion, these will be returned to the original sample. Generally, the residue after acid treatment is sufficiently pure to be weighed as silica without the hydrofluoric acid and sodium carbonate treatment.

### 3. Interferences

No interferences have been found for this method.

### 4. Definitions

Definitions found in Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water, are applicable to this method.

### 5. Apparatus

- a. Graduated cylinders.
- b. 50 ml Teflon dishes.
- c. Hot plates.
- d. #40 and #42 Whatman filter paper.

- e. Balance, 0.1 mg sensitivity.
- f. 1,000 ml Volumetric flasks.
- g. Furnace.
- h. Funnels.
- i. Platinum Crucibles.
- j. Mortar and pestle.

#### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

#### 7. Reagents

- a. Hydrochloric acid, conc.
- b. Nitric acid, conc.
- c. Perchloric acid, 70%.
- d. Hydrofluoric acid, 48%.
- e. Sodium carbonate, reagent grade.
- f. Sulfuric acid, conc.

#### 8. Sampling

Care shall be taken when sampling scales not to remove any of the metallic surface to which the scale adheres. In addition, a uniform sample shall be obtained.

#### 9. Procedure

If the sample is in water, filter through a #40 Whatman filter paper. Dry the sample at 105°C for one hour. Cool and grind the sample to pass a 100-mesh U.S. sieve. Weigh 1 g in a 50 ml Teflon dish and add 20 ml reagent water, 15 ml HCl, and 5 ml HNO<sub>3</sub>. (See Note 1, page .) Using a hot plate, heat in a hood and concentrate to 20 ml. Cool and add 20 ml HNO<sub>3</sub> and 5 ml HClO<sub>4</sub>. (CAUTION: Use the hood shield when adding HClO<sub>4</sub>.) Heat until dense HClO<sub>4</sub> fumes appear and continue heating for 10 minutes. Cool and add 5 ml HCl and 50 ml reagent water. Bring to a boil and filter through a #42 Whatman filter

paper. Wash 10 times with 1:49 HCl saving the filtrate and washings. Dilute to 1,000 ml with reagent water.

NOTE 1 - Additional acid may be required to obtain solution of the sample depending upon the concentrations of  $\text{SO}_4$ , Fe, etc.

a.  $\text{SiO}_2$  -

Place the #42 Whatman filter paper in a weighed platinum crucible. Using a Fisher burner, char without burning and heat at  $1200^\circ\text{C}$  to a constant weight. The residue is sufficiently pure to be weighed as  $\text{SiO}_2$ . If greater accuracy is desired, the residue may be volatilized with HF (plus 2 drops  $\text{H}_2\text{SO}_4$ ) and fused with  $\text{Na}_2\text{CO}_3$ . The fusion is then dissolved in HCl and added to the filtrate obtained during sample preparation.

b.  $\text{SO}_4$  -

A 250 ml aliquot of the filtrate is treated as outlined in Ch. 2, Sec. 11, Sulfates in Scale.

c. Cu -

A 10 ml aliquot, or greater if the Cu content is less than 0.004 mg, of the filtrate is treated as outlined in Ch. 2, Sec. 6, Copper in Scale.

d. Fe -

An aliquot of the filtrate is treated as outlined in Ch. 2, Sec. 9, Iron in Scale. If more than 5 mg/l Cu is present, the Cu must be removed by treatment with thioacetamide. Add 1 ml of 1M thioacetamide and let stand 1 hour. Filter through a #42 Whatman filter paper and wash with dilute HCl (10%). Save filtrate and washings for Fe determination.

e. Ca and Mg -

Calcium and magnesium are determined as outlined in Ch. 2, Sec. 4, Calcium and Magnesium in Scale. Cu will also interfere with the EDTA method for Ca and Mg. If the Cu content is greater than 2 mg/l, treat an aliquot of the filtrate with thioacetamide as outlined above.

f.  $\text{CO}_3$  -

To analyze for  $\text{CO}_3$  a sample of the scale prior to solution is used. Ch. 2, Sec. 5, Carbonate in Scale (Alkalimeter Determination), describes this analysis.

g. DTA -

Analyze a sample of the solid material as outlined in Ch. 2, Sec. 7, Differential Thermal Analysis of Scale.

h. TGA -

Analyze a sample of the solid material as outlined in Ch. 2, Sec. 12, Thermal Gravimetric Analysis of Scale.

i. Ignition Loss -

Analyze a sample of the solid material as outlined in Ch. 2, Sec. 8, Ignition Loss of Scale.

Other analyses, e.g. - Ni, Mn,  $\text{PO}_4$ , etc., may be required depending upon the origin of the sample. These analyses may be added as needed.

## SECTION 4. CALCIUM AND MAGNESIUM IN SCALE

### 1. Scope and Application

This method outlines the procedure for determining calcium and magnesium in solutions of solid materials. The method is applicable to scales or water formed deposits.

### 2. Principle of Method

Calcium and magnesium are determined in scale solutions by titrating with EDTA (ethylene diaminetetraacetic acid or its salt). The calcium will combine with EDTA first and is determined at a pH which is sufficiently high to precipitate magnesium as the hydroxide. An indicator which is specific for calcium is used. A second sample is titrated at a lower pH which allows the magnesium to remain in solution. Total hardness is determined on this sample. The magnesium content is calculated from the ml titrant used for the first sample and the total used for the second sample.

### 3. Interferences

Interferences which may be present in scale samples are Cu,  $>2 \text{ mg/l}$ ;  $\text{Fe}^{+2}$ ,  $>20 \text{ mg/l}$ ;  $\text{Fe}^{+3}$ ,  $>20 \text{ mg/l}$ ; Mn,  $10 \text{ mg/l}$ ; Zn,  $5 \text{ mg/l}$ ; Pb,  $5 \text{ mg/l}$ ; Al,  $5 \text{ mg/l}$ ; Sn,  $5 \text{ mg/l}$ . These interferences are removed in this procedure.

### 4. Definitions

Definitions found in Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water, are applicable to this method.

### 5. Apparatus

Miscellaneous glassware - Burets, pipets, flasks, etc.

## 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

## 7. Reagents

a. Thioacetamide, 1M: Dissolve 7.5 g  $\text{CH}_3\text{CSNH}_2$  in 100 ml reagent water.

b. Ammonium Hydroxide, 6N: Dilute 400 ml conc.  $\text{NH}_4\text{OH}$  to 1 liter with reagent water.

c. Sodium Hydroxide, 1N: Dissolve 40 g NaOH in 1 liter reagent water.

d. Calvert II Indicator: Available commercially.

e. EDTA Titrant, 0.01M: Dissolve 3.723 g of disodium ethylene diamine-tetraacetate dihydrate in reagent water and dilute to 1 liter. Standardize against standard calcium solution. Adjust to 1 ml = 1 mg  $\text{CaCO}_3$ .

f. Buffer Solution: Dissolve 16.9 g  $\text{NH}_4\text{Cl}$  in 143 ml conc.  $\text{NH}_4\text{OH}$ . Add 1.25 g EDTA magnesium salt (tetraacetic acid magnesium disodium salt) and dilute to 250 ml with reagent water.

g. Eriochrome Black T Indicator: Dissolve 0.5 g dye and 4.5 g hydroxylamine hydrochloride in 100 ml 95% ethyl alcohol.

h. Standard Calcium Solution: Weigh 1.0000 g anhydrous calcium carbonate into a 500 ml erlenmeyer flask. Add 1:1 HCl dropwise until the  $\text{CaCO}_3$  has dissolved. Add approximately 200 ml reagent water and boil 5 minutes. Cool and add 3 drops methyl red indicator. Adjust the pH by adding either 6N  $\text{NH}_4\text{OH}$  or 1:1 HCl as required until the solution color is orange. Transfer to a 1 liter volumetric flask and dilute to the mark with reagent water. One (1) ml of this solution is equivalent to 1 mg  $\text{CaCO}_3$ .

## 8. Sampling

Care shall be taken when sampling scales not to remove any of the metallic surface to which the scale adheres. In addition, a uniform sample shall be obtained. Prepare the sample for analysis as outlined in Ch. 2, Sec. 3, Preparation and Analysis of Scale.

## 9. Procedure

### a. Calcium -

Dilute 5 ml of the scale solution to 10 ml with reagent water. Add 1 ml of the 1M thioacetamide solution and heat without boiling. Filter through a #42 Whatman filter paper. Make alkaline with 6N  $\text{NH}_4\text{OH}$  and heat without boiling. Filter through a #1 Whatman filter paper and add 1N NaOH to a pH greater than 12. Dilute to 50 ml with reagent water. Add 1 scoop (scoop furnished with indicator) Calvert II indicator and titrate with 0.01M EDTA. The color change at the end point is red to blue.

### b. Total hardness -

Dilute 5 ml of the scale solution to 10 ml with reagent water. Add 1 ml of the 1M thioacetamide solution and heat without boiling. Filter through a #42 Whatman filter paper. Add the buffer solution dropwise to pH 10 (see Note 1) and heat without boiling. Filter through a #1 Whatman filter paper and dilute to 50 ml with reagent water. Add 1/2 ml Eriochrome Black T indicator and titrate with 0.01M EDTA to the blue end point.

NOTE 1 - Do not add more than 2 ml buffer solution.

## 10. Calculations

### 1. Calcium -

$$\text{mg/l (ppm) Ca} = \frac{\text{ml EDTA} \times 400.4 \times f}{\text{ml sample}}$$

$$f = \frac{\text{mg CaCO}_3}{\text{ml EDTA}}, \text{ where } 0.01\text{M EDTA is used, } f = 1$$

### 2. Total hardness as mg/l $\text{CaCO}_3$ -

$$\text{mg/l (ppm) CaCO}_3 = \frac{\text{ml EDTA} \times 1,000 \times f}{\text{ml sample}}$$

### 3. Magnesium -

$$\text{mg/l (ppm) Mg} = \frac{\text{ml EDTA (total hardness)} - \text{ml EDTA (Ca)} \times 243}{\text{ml sample}}$$

## 11. Precision and Accuracy

Precision and accuracy are governed by sample size and buret graduations.

## SECTION 5. CARBONATE IN SCALE

### (Alkalimeter Determination)

#### 1. Scope and Application

This method outlines the determination of carbonate in solid materials. The method is applicable to scales or water formed deposits which are to be analyzed for constituents other than organics or carbonaceous materials.

#### 2. Principle of Method

When concentrated hydrochloric acid is added to scale containing carbonate, carbon dioxide is evolved. The weight loss of the sample is proportional to the amount of carbonate present.

#### 3. Interferences

This method is essentially free of interferences when analyzing scale.

#### 4. Definitions

Definitions found in Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water, are applicable to this method.

#### 5. Apparatus

- a. Drying oven for use at 105° C.
- b. Desiccator.
- c. Analytical balance with sensitivity of 0.1 mg.
- d. Alkalimeter - Schroetter.

#### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

## 7. Reagents

- a. Hydrochloric Acid - concentrated.
- b. Reagent water.

## 8. Sampling

Care shall be taken when sampling scales not to remove any of the metallic surface to which the scale adheres. In addition, a uniform sample shall be obtained.

## 9. Procedure

Thoroughly clean and dry the alkalimeter. Cool in a desiccator. Grind a sample of the scale to pass a 100-mesh U.S. sieve. Dry at 105°C for 1 hour and cool in a desiccator. Weigh 1 g of the sample. (See Note 1.) Add the weighed sample and enough reagent water to suspend it (approximately 5 ml) to the alkalimeter. (See Note 2.) Fill the acid reservoir of the alkalimeter with conc. HCl. Weigh the alkalimeter and its contents. Slowly add the HCl and allow the CO<sub>2</sub> to escape by opening the alkalimeter vent. (CAUTION: Rapid addition of HCl to large amounts of carbonate will result in a violent reaction.) Continue addition of the HCl until the reaction stops. Shake to insure that the reaction is complete. (See Note 3.) Weigh the alkalimeter and its contents.

NOTE 1 - All weights are made to the nearest 0.1 mg.

NOTE 2 - Add sample and reagent water through bottom opening of alkalimeter. Always replace stopper after addition.

NOTE 3 - If additional HCl is required, the reservoir may be refilled and the alkalimeter reweighed. Weight of the alkalimeter before filling must be known.

## 10. Calculations

Grams CO<sub>2</sub> = Original weight of alkalimeter and contents minus final weight of alkalimeter and contents.

If additional HCl was required, its weight must be added to the original weight.

$$\text{Grams Carbonate} = \text{Grams CO}_2 \times 1.36$$

## 11. Precision and Accuracy

With proper technique, the analyst can reproduce his results within  $\pm 1$  ppm.

## SECTION 6. COPPER IN SCALE

### 1. Scope and Application

This method outlines the procedure for determining copper in solutions of solid materials. The method is applicable to scales or water formed deposits.

### 2. Principle of Method

Two (2) moles of 2,9-dimethyl - 1,10-phenanthroline (neocuproine) will react with 1 mole of cuprous ion to form an orange complex. The complex is extracted with a chloroform-isopropyl alcohol mixture and the absorbance is read at 457 m $\mu$ . The color obeys Beer's Law in concentrations up to 0.2 mg Cu per 25 ml of solvent. A pH between 3 and 9 in the aqueous system allows full color development. The color is stable in the chloroform-isopropyl alcohol mixture for several days. The minimum detectable concentration using this procedure is 0.002 mg Cu.

### 3. Interferences

In scales, this method is essentially free of interferences.

### 4. Definitions

Definitions found in Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water, are applicable to this method.

### 5. Apparatus

- a. Spectrophotometer - for use at 457 m $\mu$ .
- b. 125 ml separatory funnels.
- c. 25 ml volumetric flasks.

### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

In addition, for this analysis reagent water shall mean distilled water which has been deionized or redistilled using glass apparatus to give copper-free water.

## 7. Reagents

a. Copper Stock Solution: Dissolve 0.2000 g of polished electrolytic copper wire in 10 ml of reagent water and 5 ml concentrated  $\text{HNO}_3$ . After the reaction has slowed, warm gently to complete solution and then boil to expel nitrogen oxides. Cool and add 50 ml of reagent water. Transfer to a 1 liter volumetric flask and dilute to the mark with reagent water. This solution contains 0.200 mg Cu per ml.

b. Standard Copper Solution: Dilute 50 ml of the stock solution to 500 ml with reagent water. One (1) ml of this solution contains 0.02 mg Cu.

c. Hydroxylamine Hydrochloride Solution: Dissolve 50 g of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  in 450 ml reagent water.

d. Nitric Acid, 1:9: Add 1 volume concentrated  $\text{HNO}_3$  to 9 volumes reagent water. This mixture is used for cleaning glassware.

e. Sodium Citrate Solution: Dissolve 150 g  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$  in 400 ml reagent water. Add 5 ml  $\text{NH}_2\text{OH} \cdot \text{HCl}$  solution, 10 ml neocuproine, and 50 ml chloroform. Discard the chloroform layer which contains any Cu impurities that may have been present.

f. Ammonium Hydroxide Solution, 6N: Dilute 400 ml concentrated ammonium hydroxide to 1 liter with reagent water and store in a polyethylene bottle.

g. Neocuproine Reagent: Dissolve 0.1 g of neocuproine in 100 ml methanol. Stability of this solution is at least 1 month.

h. Chloroform - reagent grade.

i. Isopropyl Alcohol - reagent grade.

j. pH Paper - range 4 - 6.

## 8. Sampling

Care shall be taken when sampling scales not to remove any of the metallic surface to which the scale adheres. In addition, a uniform sample shall be obtained. Prepare the sample for analysis as outlined in Ch. 2, Sec. 3, Preparation and Analysis of Scale.

## 9. Calibration and Standardization

Prepare a series of standards (0.002 to 0.10 mg Cu) using the standard copper solutions. Dilute to 100 ml with reagent water and develop the color as outlined under Procedure. Measure the absorbance and plot against mg Cu. If chloroform is used as reference, the absorbance values must be corrected by subtracting the absorbance of a reagent blank. For smaller amounts of copper, a calibration curve may be prepared by diluting 10 ml of the standard copper

solutions to 100 ml and carrying 1 to 10 ml volumes through the described procedure. Use of a larger sample cell in the spectrophotometer will be required to increase sensitivity.

#### 10. Procedure (See Note 1)

Pipet 25 ml of the sample or an aliquot containing 0.004 - 0.2 mg Cu into a 125 ml separatory funnel. Dilute to 10 ml with reagent water if necessary. Add 5 ml hydroxylamine hydrochloride solution and 10 ml sodium citrate solution. Mix thoroughly and then adjust the pH to 4 - 6 with the 6N ammonium hydroxide or 1:9 nitric acid. (pH test paper showing a color change in the 4 - 6 range may be used as the indicator.)

Add 10 ml neocuproine reagent and 10 ml chloroform. The complex is extracted into the chloroform by stoppering the separatory funnel and shaking for 30 seconds. Allow the mixture to separate and then add the chloroform layer to a 25 ml volumetric flask. (See Note 2.) The extraction of the water layer is repeated using 5 ml chloroform. This extract is added to the previous one. Dilute the extracts to 25 ml using isopropyl alcohol. Stopper and mix thoroughly. A portion of the solution is transferred to a suitable absorption cell, and the absorbance is measured at 457 m $\mu$  using a spectrophotometer. Chloroform or 10 ml of reagent water treated as the sample is used as a reference.

NOTE 1 - All glassware must be thoroughly cleaned. Soaking of sample bottles and other glassware in hot 1:9 HNO<sub>3</sub> for several hours is recommended.

NOTE 2 - Add approximately 10 ml isopropyl alcohol to each volumetric flask prior to addition of the extract.

#### 11. Calculations

The ppm Cu is determined by comparison of observed absorbance with the calibration curve and using the following equation:

$$\text{mg/l (ppm) Cu} = \frac{\text{mg Cu (from curve)} \times 1,000}{\text{ml aliquot}}$$

#### 12. Precision and Accuracy

Precision and accuracy depend on the sample size and size of cell used with the spectrophotometer. Results can be reproduced to 0.002 mg Cu.

## SECTION 7. DIFFERENTIAL THERMAL ANALYSIS OF SCALE

### 1. Scope and Application

This method outlines the procedure for determining compounds in solid materials by differential thermal analysis. The method is applicable to scales or water formed deposits.

### 2. Principle of Method

Differential thermal analyzers are designed to detect and record energy changes in the form of heat released from or absorbed by a material being heated or cooled over a specified temperature range. The differential thermocouple detection system consists of two thermocouples connected in series-opposition, a high gain amplifier, and a recorder. The sample to be analyzed is placed on one of the thermocouples, and on the opposing thermocouple, an inert material is placed as a reference. If the temperatures of the sample and reference materials are raised or lowered equally during heating or cooling, the thermocouples cancel out the generated EMF. However, should a sample reaction occur in which heat is released or absorbed, the sample thermocouple will produce an EMF greater or less than the reference thermocouple. This signal is amplified and sent to the recorder. The resulting plot of the sample's thermal characteristics is called a thermogram.

### 3. Interferences

Various compounds will cause shifts in peaks of other compounds on the thermogram. This interference can be compensated for by using mixtures of expected or known compounds as standards. A chemical analysis of the sample to determine the cation and anion composition is essential for interpretation of the thermogram in many cases. Variables which effect the thermogram are divided into two (2) general categories — (a) instrumental factors and (b) sample characteristics. Instrumental factors include —

- a. Furnace atmosphere
- b. Furnace size and shape
- c. Sample holder material
- d. Sample holder geometry
- e. Wire and bead size of thermocouple junction
- f. Heating rate
- g. Differential temperature setting
- h. Speed and response of recording instrument

- i. Thermocouple location with respect to the sample and reference
- j. Thermocouple geometry
- k. Overall sensitivity of the instrument

Most of the instrumental factors which effect the thermogram are inherent to the instrument. However, the location of the thermocouple with respect to sample and reference depends in large part on the technique of the analyst as does the geometry of the thermocouple.

Sample characteristics which effect the thermogram are covered in paragraph 9a of this method.

#### 4. Definitions

Definitions found in Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water, are applicable to this method.

#### 5. Apparatus

- a. Differential Thermal Analyzer - Manufacturers include Premco, DuPont, Mettler, Stone, and Fisher.
- b. Mortar and Pestle
- c. Oven - to 105°C
- d. Desiccator
- e. Plastic Petri Dishes

#### 6. Purity of Reagents

Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

#### 7. Reagents

- a. Aluminum Oxide,  $\text{Al}_2\text{O}_3$
- b. Other compounds as desired for preparing standards.

#### 8. Sampling

Care shall be taken when sampling scales not to remove any of the metallic surface to which the scale adheres. In addition, a uniform sample shall be obtained.

## 9. Procedure

### a. Preparation of Sample

The sample should be dried at 105°C to remove free water. Grind the sample with a mortar and pestle to get a homogeneous mixture of uniform particle size. Sieves may be used to size the sample. Store the sample in a desiccator until the analysis is to be made. The following sample characteristics will affect the thermogram:

- (1) Particle size
- (2) Thermal conductivity
- (3) Heat capacity
- (4) Swelling or shrinkage of sample
- (5) Amount of sample
- (6) Effect of diluent
- (7) Degree of crystallinity

The reference material should have thermal characteristics (specific heat, heat conductivity, thermal diffusivity) as closely equal as possible to those of the sample material. In addition, the particle size and amount of reference material should approximate that of the sample. Particle size and amount are two characteristics of the sample and reference which can be controlled to some degree by the analyst. Other characteristics cannot be controlled.

### b. Analysis of Sample

A procedure for analyzing samples will not be given in this method. The procedure will vary with the instrument used and the atmospheric conditions of the analysis. Atmospheric conditions may be varied from normal to pressurized, vacuum, and inert gas.

Table I is a list of physical and chemical phenomena and the enthalpic changes which occur when these phenomena are subjected to heat. Differential thermal analysis will detect these changes.

DTA has been used to determine the composition of scales. Various forms of calcium sulfate (anhydrous, hemihydrate, dihydrate) have been identified in addition to carbonates, hydroxides, and oxides of calcium, magnesium, iron, and copper.

## 10. Calculations

For qualitative results, no calculations are necessary. Compounds indicated on the thermogram are verified by consulting references and standards. Quantitative results require known sample weights and determination of peak height.

## 11. Precision and Accuracy

Due to the type of analytical data provided by this instrument, no precision and accuracy will be stated.

TABLE I  
THERMAL METHODS OF ANALYSIS

Phenomena	Enthalpic change	
	Endothermal	Exothermal
Physical		
Crystalline transition	x	x
Fusion	x	
Vaporization	x	
Sublimation	x	
Adsorption		x
Desorption	x	
Absorption	x	
Chemical		
Chemisorption		x
Desolvation	x	
Dehydration	x	
Decomposition	x	x
Oxidative degradation		x
Oxidation in gaseous atmosphere		x
Reduction in gaseous atmosphere	x	
Redox reactions	x	x
Solid-state reaction	x	x

## SECTION 8. IGNITION LOSS OF SCALE

### 1. Scope and Application

This method outlines the procedure for determining the ignition loss of solid materials. The method is applicable to scales or water formed deposits.

### 2. Principle of Method

A weighed sample of the scale is heated in a muffle furnace at a predetermined temperature for a fixed length of time. The weight loss or gain is measured by weighing the sample after ignition.

A weight loss after ignition can be attributed to such materials as organic matter, carbon, sulfur (sulfite and sulfide), carbon dioxide from carbonates, and in some cases, nitrogen oxides and ammonia. Certain hydrates may also be decomposed.

The results of an ignition loss test are difficult to interpret however, since while some constituents are being driven away, others are being oxidized to higher weight values. For example, reduced forms of iron oxide and copper can increase in weight on ignition.

The ignition loss test will assist the analyst in confirming the presence of constituents indicated by other tests. For example, if the presence of a large amount of copper has been confirmed by a previous test, a proportionate increase in weight on ignition will be expected. The presence of a large amount of organics would indicate that the analyst can expect a large weight loss on ignition.

Heating to a lower temperature than the usual 900°C can provide useful information in some cases. Carbonaceous samples, for example, should be heated to a maximum temperature of 500°C.

### 3. Interferences

Interferences as such are not present in this method. However, the analyst must be careful in his interpretation of results as pointed out in paragraph 2, Principle of Method.

### 4. Definitions

Definitions found in Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water, are applicable to this method.

### 5. Apparatus

- a. Muffle Furnace - for use to 1,000°C
- b. Platinum or Porcelain Crucibles

- c. Desiccator
- d. Analytical Balance - sensitivity of 0.1 mg
- e. Tongs - for handling crucibles

6. Purity of Reagents

Not applicable to this method.

7. Reagents

Not applicable to this method.

8. Sampling

Care shall be taken when sampling scales not to remove any of the metallic surface to which the scale adheres. In addition, a uniform sample shall be obtained.

9. Procedure

Dry the sample at 105°C for one hour. Cool and grind to pass a 100-mesh U.S. sieve. Store in a desiccator until the ignition loss test is to be made. Place 1 g of the sample into a previously dried platinum or porcelain crucible.

Weigh the crucible and contents and record the weight. Place the crucible in a muffle furnace which has been heated to a predetermined temperature (500°C max. for carbonaceous samples and 900°C for other samples). The length of ignition time is left to the discretion of the analyst but should be equal to or exceed 1 hour. A uniform length of ignition time for all samples is preferred and provides more meaningful data.

When the ignition time has expired, remove the crucible. Place the crucible in a desiccator to cool for at least 30 minutes. Then weigh the crucible and contents. Record this weight.

10. Calculations

Results may be reported in grams per gram of sample or percent. The following equations are used:

1. Ignition loss, grams per gram of sample = Initial weight in grams of crucible and contents minus Final weight in grams of crucible and contents.

If 1 gram of sample is used, the results are in grams per gram of sample. If less than 1 gram is used, the analyst must adjust the results to reflect the use of 1 gram.

$$2. \text{ Ignition loss, percent} = \frac{\text{Final weight of sample in grams}}{\text{Initial weight of sample in grams}} \times 100$$

#### 11. Precision and Accuracy

Due to the type of analytical results obtained with this method, the precision and accuracy cannot be given.

### SECTION 9. IRON IN SCALE

#### 1. Scope and Application

This method outlines the procedure for determining total iron in solutions of solid materials. The method is applicable to scales on water formed deposits.

#### 2. Principle of Method

Solution of iron and reduction to the ferrous state is accomplished by boiling with acid and hydroxylamine hydrochloride. Treatment with 1,10-phenanthroline yields an orange-red complex which is formed when three (3) molecules of phenanthroline chelate an atom of ferrous iron. The complex in solution obeys Beer's Law, and its intensity is independent of pH in the range 3-9, and is stable for 6 months. In the presence of excess phenanthroline, rapid color development can be obtained between pH 2.9 and 3.5. Detectable concentrations are 0.02 to 4.0 mg/l. Higher concentrations can be determined by using aliquots.

#### 3. Interferences

Interferences include phosphates (poly greater than ortho), chromium, zinc in concentrations exceeding ten (10) times that of iron, copper and cobalt in excess of 5 mg/l, nickel in excess of 2 mg/l, bismuth, silver, cadmium, mercury, and molybdate, which are precipitated by phenanthroline. Boiling with acid eliminates interfering polyphosphates by reversion to ortho. This step also eliminates interfering cyanides and nitrites. Interferences caused by excessive concentrations of strong oxidizing agents are eliminated by adding more hydroxylamine hydrochloride. Color and organic matter may be removed by evaporation, ashing, and redissolving in acid.

#### 4. Definitions

Definitions of terms used are given in this report under Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water.

## 5. Apparatus

- a. Spectrophotometer for use at 510 mμ.
- b. 1, 2, 10, and 50 ml pipets.
- c. 50 ml volumetric flasks.
- d. 125 ml erlenmeyer flasks.

## 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water." In addition, for this analysis reagent water shall mean distilled water that has been deionized to give iron free water.

## 7. Reagents

Hydroxylamine hydrochloride and phenanthroline solutions are stable for several months. Working iron solutions should be prepared from stock solution as needed. Other solutions are stable indefinitely.

a. Hydrochloric Acid, conc. 37%

b. Hydroxylamine Hydrochloride: Dissolve 10 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  in 100 ml of reagent water.

c. Ammonium Acetate Buffer Solution: Dissolve 250 g  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  in 150 ml reagent water. Add 700 ml glacial acetic acid and dilute to 1 liter with reagent water.

d. Phenanthroline Solution: Dissolve 0.1 g 1,10-phenanthroline monohydrate,  $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$ , in 100 ml reagent water with 2 drops conc. HCl added. Solution must be clear. One (1) ml of this reagent is sufficient for no more than 0.1 mg Fe.

e. Iron Stock Solution: Clean electrolytic iron wire with sandpaper to produce a bright surface. Weigh 0.2000 g and dissolve in 6N  $\text{H}_2\text{SO}_4$ . Dilute to 1 liter with reagent water. This solution contains 0.20 mg Fe per ml. Ferrous ammonium sulfate can be used to prepare the stock solution by dissolving 0.7022 g in 20 ml conc.  $\text{H}_2\text{SO}_4$  and 50 ml reagent water. Add 0.1N  $\text{KMnO}_4$  until a faint pink persists and dilute to 1 liter. This solution contains 0.10 mg Fe per ml.

7. Iron Working Solution: Prepare daily from stock solution as needed. Dilute 50 ml of iron wire stock solution or 100 ml ferrous ammonium sulfate stock solution to 1 liter with reagent water. This solution contains 0.010 mg Fe per ml. Dilute 5 ml of iron wire stock solution or 10 ml ferrous ammonium sulfate stock solution to 1 liter. This solution contains 0.001 mg Fe per ml.

#### 8. Sampling

Care shall be taken when sampling scales not to remove any of the metallic surface to which the scale adheres. In addition, a uniform sample shall be obtained. Prepare the sample for analysis as outlined in Ch. 2, Sec. 3, Preparation and Analysis of Scale.

#### 9. Calibration and Standardization

Prepare a series of standards, ranging from 0.001 to 0.10 mg Fe, by accurately pipeting calculated volumes of working solutions into 125 ml erlenmeyer flasks using the weaker working solution (0.001 mg per ml) to prepare the 0.001-0.010 mg standards. Dilute to 50 ml and treat as described in the procedure for total iron. The standards are read against reagent water set at zero absorbance and a calibration curve plotted, including a blank (reagent water treated to correct for iron in the reagent water and reagents). If color or turbidity interfere, samples can be taken through all the steps of the procedure except addition of phenanthroline. Each developed sample, with phenanthroline, is read against the corresponding blank without phenanthroline.

#### 10. Procedure

Copper is removed by treating an aliquot with 5 ml hydroxylamine hydrochloride solution (10 g in 100 ml reagent water), 10 ml sodium citrate solution (30 g in 80 ml reagent water, and 10 ml neocuproine solution (0.1 g in 100 ml methanol) and extracting the neocuproine complex with chloroform. Treat an aliquot of the water layer as described below. Correct for dilution caused by the addition of reagents to remove copper.

Mix the sample thoroughly and pipet 10 ml or an aliquot containing not more than 0.1 mg Fe into a 125 ml erlenmeyer flask. Dilute to 50 ml if necessary and add 2-5 drops conc. HCl and 1 ml hydroxylamine hydrochloride solution. Add glass beads and reduce volume to 15-20 ml by boiling. Cool to room temperature and transfer to a 50 ml volumetric flask. Add 10 ml acetate buffer solution and 2 ml phenanthroline solution. Dilute to the mark with reagent water, mix thoroughly, and allow 10 minutes for maximum color development. Measure the absorbance on a spectrophotometer set at 510 mμ.

## 11. Calculations

The ppm Fe is determined by comparison of observed readings with the calibration curve and using the following equation:

$$\text{mg/l (ppm) Fe} = \frac{\text{mg Fe (from curve)} \times 1,000}{\text{ml sample}}$$

## 12. Precision and Accuracy

Using a spectrophotometer, the reliability of this method is approximately 1 percent of 0.001 mg whichever is the greater. Results can be reproduced to within 0.02 ppm.

# SECTION 10. SILICA IN SCALE

The method for determining silica in scale and water formed deposits is outlined in Ch. 2, Sec. 3, Preparation and Analysis of Scale.

# SECTION 11. SULFATES IN SCALE

## 1. Scope and Application

This method outlines the procedure for determining the sulfate concentration in solutions of solid materials. The method is applicable to scales or water formed deposits where the sulfate concentration exceeds 10 mg/l.

## 2. Principle of Method

In an acid medium when barium chloride is added, sulfates are precipitated as barium sulfate. The precipitate is dried and weighed as barium sulfate. The sulfate concentration is calculated from this weight.

## 3. Interferences

Interferences include suspended matter, silica, sulfites, sulfides, and nitrates. These interferences lead to high results. Low results can be caused by iron, chromium, or other heavy metals. Suspended matter and silica interferences are removed in this method. Barium sulfate tends to occlude or adsorb other interferences; however, the precision and accuracy of the method is not significantly affected.

#### 4. Definitions

Definitions found in Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water, are applicable to this method.

#### 5. Apparatus

- a. Drying oven for use at 80 - 90°C.
- b. Muffle furnace for use at 800°C.
- c. Desiccator.
- d. Gooch crucibles and suction apparatus.
- e. Analytical balance with sensitivity of 0.1 mg.
- f. Hot plate.
- g. Miscellaneous glassware.
- h. Ashless filter paper.
- i. Platinum crucibles.

#### 6. Purity of Reagents

a. Reagent grade chemicals shall be used unless otherwise indicated. The chemicals shall comply with specifications outlined by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

b. Reagent water shall conform to the specifications outlined in ASTM Designation: D1193, "Specifications for Reagent Water."

#### 7. Reagents

- a. Hydrochloric Acid, 1:9: Add 1 volume concentrated HCl to 9 volumes reagent water.
- b. Methyl Orange Indicator: Dissolve 0.05 g of methyl orange in 100 ml of reagent water.
- c. Barium Chloride Solution: Dissolve 100 g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in one liter of reagent water. Filter through a #40 Whatman filter paper. One (1) ml of this solution will precipitate approximately 40 mg  $\text{SO}_4$ .
- d. Asbestos for Filter Mat: Add 15 g acid-washed medium-filter asbestos to 1 liter of reagent water. Remove the fines by decantation.
- e. Chloride Test Solution: Dissolve 8.5 g  $\text{AgNO}_3$  and 0.5 ml concentrated  $\text{HNO}_3$  in 500 ml reagent water.

- f. Hydrofluoric Acid, concentrated.
- g. Sulfuric Acid, concentrated.
- h. Picric Acid, saturated aqueous solution.

## 8. Sampling

Care shall be taken when sampling scales not to remove any of the metallic surface to which the scale adheres. In addition, a uniform sample shall be obtained. Prepare the sample for analysis as outlined in Ch. 2, Sec. 3, Preparation and Analysis of Scale.

## 9. Procedure

Interfering cations are removed by passing the sample through a cation removing ion-exchange column. Suspended matter is removed by filtering. Silica in excess of 25 mg per liter is removed as described in the procedure. A 250 ml aliquot of the scale solution is placed in a 400 ml beaker. Heat the solution to boiling and while stirring vigorously, slowly add hot  $\text{BaCl}_2$  solution (see Note 1) until precipitation appears to be complete. Then add 2 ml excess.

NOTE 1 - Addition of 10 ml of the saturated picric acid solution and boiling before adding the  $\text{BaCl}_2$  solution will speed up precipitation and produce a coarser precipitate.

Allow the sample to digest at 80 - 90°C for at least 2 hours, preferably overnight.

An asbestos filter mat in the Gooch crucible is prepared using suitable suction apparatus. Wash with hot reagent water, dry, and ignite at 800°C for 30 minutes. Cool the crucible in a desiccator and weigh.

Using the Gooch crucible, filter the  $\text{BaSO}_4$  suspension. Wash the precipitate with hot reagent water until the washings are substantially free of chlorides as indicated by the  $\text{AgNO}_3$  solution. (See Note 2.)

NOTE 2 - Complete elimination of chlorides by washing should not be attempted. Discontinue washing when the  $\text{AgNO}_3$  solution produces no more than a faint opalescence.

Dry the filter and precipitate and ignite at 800°C for 30 minutes. Cool in a desiccator and weigh.

If silica is present in concentrations exceeding 25 mg/l, the  $\text{BaSO}_4$  suspension is filtered using an ashless filter paper instead of a Gooch crucible. The filter paper is charred in a weighed platinum crucible and ignited at 800°C for 1 hour.

Add 1 drop concentration  $\text{H}_2\text{SO}_4$  and 5-8 drops of HF to the residue and evaporate under a hood to expel silica as  $\text{SiF}_4$ . Reignite at  $800^\circ\text{C}$  for 30 minutes, cool in a desiccator, and weigh as  $\text{BaSO}_4$ .

#### 10. Calculations

The concentration of  $\text{SO}_4$  ion in ppm is calculated using the following equation:

$$\text{mg/l (ppm) SO} = \frac{\text{mg BaSO}_4 \times 411.5}{\text{ml sample}}$$

#### 11. Precision and Accuracy

Precision and accuracy depend on the technique of the individual analyst. With proper technique, results can be reproduced to within 10 ppm when analyzing scale.

### SECTION 12. THERMOGRAVIMETRIC ANALYSIS OF SCALE

#### 1. Scope and Application

This method outlines the procedure for determining the weight loss or gain of compounds in solid materials by thermogravimetric analysis. The method is applicable to scales or water formed deposits.

#### 2. Principle of Method

Thermogravimetric analysis provides a means of obtaining information concerning the thermal stability and composition of an original sample, the composition and thermal stability of intermediate compounds, and the composition of the residue. This information is obtained by continuously measuring the weight or weight change of a sample as it is subject to heat at a constant, linear rate. The resulting curve, weight change versus temperature, is called a thermogram or thermogravigram.

Weight changes resulting from decomposition, loss of combined water, oxidation, reduction, etc. are measured. The analyst may also obtain useful data by varying the furnace atmosphere from normal to pressurized, vacuum, oxidizing, or nonoxidizing.

The information gained by thermogravimetric analysis is most significant when evaluated in conjunction with a differential thermal analysis of the same sample. With TGA and DTA thermograms, the analyst can obtain both qualitative and quantitative results. In some cases, additional analytical data such as that

provided by gas chromatography, mass spectrometry, X-ray diffraction, etc. may be required for complete interpretation of results.

### 3. Interferences

Various compounds will cause shifts in peaks of other compounds on the thermogram. However, this does not normally affect the weight change of a reaction.

### 4. Definitions

Definitions found in Ch. 1, Sec. 1, Definitions of Terms Relating to Sea Water, are applicable to this method.

### 5. Apparatus

a. Thermogravimetric Analyzer - manufacturers include Cahn, DuPont, Mettler, Stone, and Fisher.

b. Mortar and Pestle.

c. Oven - for use at 105°C.

d. Desiccator.

e. Plastic Petri Dishes.

### 6. Purity of Reagents

Not applicable to this method.

### 7. Reagents

Not applicable to this method.

### 8. Sampling

Care shall be taken when sampling scales not to remove any of the metallic surface to which the scale adheres. In addition, a uniform sample shall be obtained.

### 9. Procedure

#### a. Preparation of Sample

The sample should be dried at 105°C to remove free water. Grind the sample with a mortar and pestle to get a homogeneous mixture of uniform particle size. Sieves may be used to size the sample. Store the sample in a desiccator until the analysis is to be made.

## b. Analysis of Sample

A procedure for analyzing samples will not be given in this method. The procedure will vary with the instrument used and the atmospheric conditions of the analysis. Atmospheric conditions may be varied from normal to pressurized, vacuum, and inert gas.

## 10. Calculations

Quantitative results may be obtained by thermogravimetric analysis when the composition of the sample has been identified by differential thermal analysis and/or wet chemical analysis. The weight loss or weight gain of the sample versus the temperature is used to calculate the percentages of sample constituents. For example, cupric sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) will lose its five (5) molecules of water at three (3) different temperatures. The molecules of water are lost in steps of two (2), two (2), and one (1). The initial weight of the sample, the molecular weight of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and the weight loss are used to determine the percentage of the sample as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The following is a typical calculation:

Main constituent -  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Initial weight of sample - 11.5 mg

Total weight loss - 4.0 mg

Molecular weight of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  - 249.60

% water (combined) - 3.61

$$\% \text{ weight loss} = \frac{\text{Weight loss}}{\text{Initial sample weight}} = \frac{4.0 \text{ mg}}{11.5 \text{ mg}} = 3.48$$

$$\% \text{ CuSO}_4 \cdot 5\text{H}_2\text{O} \text{ in sample} = \frac{\% \text{ weight loss}}{\% \text{ actual water in CuSO}_4 \cdot 5\text{H}_2\text{O}} = 96.39$$

## 11. Precision and Accuracy

Due to the type of analytical data provided by thermogravimetric analysis, no precision and accuracy will be stated.

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